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Process Technology Background for Environmental Assessment/Systems Analysis Utilizing Residual Fuel Oil

Catalytic, Inc, Charlotte, N C

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

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PROCESS TECHNOLOGY BACKGROUND FOR ENVIRONMENTAL ASSESSMENT/SYSTEMS ANALYSIS UTILIZING RESIDUAL FUEL OIL

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by

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CONTENTS

Figures iii
Tables iv
Abbreviations and Symbols v
1. Executive Summary 1
2. Introduction 4
3. Annual Summary of Environmental Assessment by Task 6
4. Residual Oil Gasification Process 11
5. Direct Hydrodesulfurization 30
6. Flue Gas Desulfurization 40
7. Conclusions 64
Glossary 68

FIGURES

Number		Page
1	Environmental assessment diagram	9
2	Shell Gasification Process	15
3	Shell Closed Carbon Recovery System	16
4	Selexol H_2S removal process	17
5	Straight through CLAUS process	18
6	Shell Claus Off-Gas Treating (SCOT) process	19
7	Typical residual oil gasification unit (POX)	21
8	Typical gasification cleanup unit for (POX)	22
9	Direct hydrodesulfurization unit operations	33
10	HDS entering and exiting streams	34
11	Material balance for Shell HDS unit	35
12	Double alkali process - ammonia absorbent	43
13	Dowa $Al_2(SO_4)_3 \cdot Al_2O_3$ absorbent - double alkali process	46
14	Limestone slurry scrubbing throwaway process	47
15	Test run on FGD unit using MgO	50
16	Double alkali process - sodium acetate-absorbent	58
17	Sulfur dioxide reduction trends in Japan	59

TABLES

Number		Page
1	Description of Flow from Figures 7 & 8	23
2	Summary of Potential Pollutants	24
3	Typical Feeds and Products	25
4	Weight Balance for Process (Air Oxidant)	26
5	Energy Balance for Process (Air Oxidant)	27
6	Potential Pollutant Streams	28
7	Total Costs of Producing 2.35 x 10^9 BTU/HR (LHV) of Product Gas	29
8	Commercial Direct HDS Facilities	31
9	Tail-Gas Treatment on Commercial Units	38
10	Major Wet-Type Flue Gas Desulfurization Processes	43
11	Development of Commercial FGD Processes	44
12	Wastewater from FGD Plants	52
13	Comparison of Design and Operating Parameters Versus Performance	54-55
14	Environmental Pollutant Control Capabilities of Residual Oil-Fired Boiler Flue Gas Cleaning Processes	57
15	Ambient Air Quality Standards	60
16	NO_x Emission Standard (ppm)	61
17	Plant Cost in Battery Limits	62
18	FGD Cost by Wet-Lime Gypsum Process in Japan (1975$)	63
19	U. S. Battery Limits Capital Investment and Annual Costs	64

LIST OF ABBREVIATIONS AND SYMBOLS

CW	= cooling water
HDS	= hydrodesulfurization
POX	= partial oxidation
CAFB	= chemically active fluid bed
FGD	= flue gas desulfurization
ROSE	= residual oil solvent extraction
Btu	= British thermal units
SCF	= standard cubic feet
SCFM	= standard cubic feet per minute (60^{o}F, 1 atm.)
SCFMD	= standard cubic feet per minute - dry basis
HHV	= higher heating value
LHV	= lower heating value
LSFO	= low sulfur fuel oil
UOP	= Universal Oil Products
ppm	= parts per million
ppm(v)	= parts per million by volume
GR	= grains
NSPS	= new source performance standard
Eff.	= efficiency
T/hr.	= metric tons per hour
L/G	= liquid/gas ratio
$Nm^3/hr.$	= normal cubic meters/hour
KW	= kilowatts
MW	= megawatts
SV	= space velocity
SS	= suspended solids
bbl.	= barrels (42 U.S. gallons)

SECTION 1

EXECUTIVE SUMMARY

OBJECTIVE

The objective of the work reported here is to execute an environmental assessment from a systems analysis of the present commercially operating processes capable of using residual fuel oil to generate electricity. The processes under study include:

1. Pretreatment - Hydrodesulfurization (HDS) processing removes sulfur and other pollutants from fuel oil prior to combustion.
2. Conversion - Partial oxidation (POX) and chemically active fluidized bed (CAFB) processing convert residual fuel to an environmentally acceptable gas, which can be used directly or in a combined cycle system.
3. Post-treatment - Flue gas desulfurization (FGD) techniques remove pollutants by cleaning the tail-gas from conventional boiler combustion.

RESULTS OVERVIEW

The status of the environmental assessment project is presented in this report, where all existing data has been compiled on residual fuel oil processes. An intensive study of three major control processes was required for the assessment of present commercial technology.

The information obtained on the processes was reviewed for a detailed engineering and cost analysis. At the present time, several economic studies are being conducted for commercial partial oxidation schemes. Five FGD systems and four HDS processes have been reviewed. A study of the combined cycle units has been started and is being continued. The commercial status of

the processes under study shows that there are numerous units now in operation having significant capacities and operating experience.

The emissions of representative commercial HDS, FCD, and FOX units were identified and characterized. Each process was analyzed in terms of basic unit operations. An overall material balance was then made for typical feed to determine the quantity of each emission based on the feed and pollutant element under consideration. From the material balance, each pollutant could be followed through the process to its final form and point of environmental impact.

Residual fuel oil contains hydrocarbons and certain contaminants such as sulfur, ash, and metals. These contaminants can be potential pollution problems as they are transferred in different forms to the media from each of the processes.

Sulfur data is well defined on all H_2S and SO_2 removal processes. However, very little data is available on other potential pollutants including vanadium, nickel, NO_x, ash, particulates, carcinogens, etc. All important emission levels from the process units have been calculated; however, it will be necessary to analyze samples from various cleanup processes in order to determine present and future emission levels. No problems are anticipated with excess pollution from sulfur in the effluent gas from these processes.

Investment costs and operating requirements have been used to estimate the control costs and efficiencies. Data collected on the trip to Japan were helpful in making these estimates and in obtaining missing information on commercial HDS, FCC and FCD processes. Secrecy agreements have been entered into with several major companies to assist in developing this information. Some missing information still exists in the area of treatment and final disposal of some effluent streams, which contain important pollutants such as metals, carbon, ash, etc. Further plant visits will be required to obtain samples of these streams. Samples from plants will be analyzed to determine the potential pollution products. The necessity of a sampling program for each process is unquestionable. An order of magnitude estimate by engineering calculation would perhaps suffice in some cases; however, emission data is required through sampling to complete the environmental assessment.

CONCLUSIONS

It is concluded that each process under study is established as an economically acceptable unit by operating experience on a commercial scale. The flexibility of each process has been demonstrated by a proven acceptance of variable feedstocks within certain design limits.

Contaminates such as sulfur, nickel, and vanadium are successfully removed from the fuel and in some cases may be used for the production of saleable byproducts. Additional process equipment is required in most cases to upgrade byproducts to a final form. At least eighty to ninety percent removal efficiencies have been demonstrated for most contaminants. Sulfur removal efficiencies of 95 to 99% are common in FGD processes.

The capital and operating cost estimates indicate that the price for these processes is high for the U.S.A. presently. The process cost is very sensitive to feed composition. It should become more economical in the future to charge heavier lower-priced feeds into the FOX process, middle-range feeds into the HDS process, and low sulfur fuel oils for the FGD units.

SECTION 2

INTRODUCTION

In May, 1976, Catalytic, Inc. began environmental and economic assessments of methods utilizing or those capable of utilizing residual oil to produce electricity. The methods were classified by state of development into one of three phases of work.

Phase I: Processes, such as hydrodesulfurization (HDS), flue gas desulfurization (FGD) and partial oxidation (POX), which are operating or in commercial design.

Phase II: Processes, such as Chemically Active Fluidized Bed (CAFB), which are in the demonstration plant design but have a good chance of becoming commercially feasible during the three years of the contract.

Phase III: Processes, such as residual oil solvent extraction (ROSE), which are in the pilot plant phase of development.

The effort during this first year (May, 1976 - May, 1977) has been the assessment of the Phase I processes. This report presents the information obtained, status, conclusions and recommendations for the three Phase I processes: HDS, FGD and POX. We have, however, begun preparation of the work plan for the Phase II assessment of CAFB.

Descriptions of the partial oxidation, hydrodesulfurization, and flue gas desulfurization processes appear in Sections 4, 5 and 6, respectively. Since HDS and FGD are commercial and operating, the emphasis in each of these sections is on the presentation and discussion of information obtained on the units we have visited.

As part of the contract, a work plan describing six major task areas was prepared. A discussion of the work performed and status for each of these tasks appears in Section 3. Also included in Section 3 is a summary of how the process technology background reported here fits into the environmental assessment procedures.

Based on the information we have obtained and an evaluation of progress made, conclusions may be drawn as to the environmental acceptability of each process based on reported actual performance testing, calculations, and sound engineering judgement. These results were compared with six existing New Source Performance Standards (NSPS) as applied to utility boilers burning liquid fossil fuels.

The recommended steps necessary to complete the assessment are included in the environmental assessment methodology.

SECTION 3

ANNUAL SUMMARY OF ENVIRONMENTAL ASSESSMENT BY TASK

Task 2.0: Review and Analysis of Environmental, Engineering and Cost Data

During the past year, information has been obtained on the processes for environmentally acceptable residual fuel oil utilization. The information was reviewed for environmental data and for engineering and cost analysis. An intensive study of the three major processes - FGD, HDS, FOX - was begun, and data obtained on these processes in operating Japanese plants were analyzed. At the present time, several economic studies are being conducted for commercial partial oxidation schemes; five FGD systems and four HDS processes are being reviewed. A study of the combined cycle units has been started and is being continued.

Task 3.0: Identification of Important Pollutants and Projection of Attainable Emission Levels

The objective of the Phase I program is to identify and characterize the emissions of representative commercial HDS, FGD, and partial oxidation units. The goal of this preliminary environmental assessment is to determine the environmental adequacy of these processes. The first step in the assessment procedure was to analyze the residual fuel oil utilization processes in terms of basic unit operation. This analysis was begun for FOX, FGD, and HDS. The next step included the identification and characterization of effluent streams for each of the various HDS, FOX, and FGD processes. Areas of potential concern have also been identified. To determine the pollutant loadings in the effluent streams, a typical overall material balance has been made for each process. After additional studies are completed, an estimate of the control efficiency will be considered as a function of costs and process operating conditions. Data collected on the trip to Japan have been analyzed and tabulated on a material balance sheet. A tabulation of investment costs

and operating requirements has been prepared and will be used to estimate control costs and efficiencies.

Task 4.0: Identification of Missing Information and Design of Program to Develop Such Information

During the past year, our efforts have been concentrated on obtaining missing information on commercial HDS, FOX, and FGD processes. In order to obtain this information, secrecy agreements have been entered into with several major companies, and visits have been made to various FGD, HDS, and FOX operating units. A trip to Japan was also made for the purpose of obtaining process, cost, and environmental data on commercial HDS, FOX, and FGD processes. The results of the survey taken in Japan indicate several areas in which additional data on commercial scale FGD systems is needed before a reliable, complete environmental analysis can be given. A test program to obtain the missing information must be designed and planned in detail with the guidance and approval of the Task Officer.

Task 5.0: Design and Execution of Source, Fugitive and Ambient Measurement Program

Based on the analysis of the results of our trip to Japan, a sampling program will be designed, using the best available information, to obtain emission data required to complete the environmental assessment. A comprehensive breadth and depth in scope of work and definition of total effort requires the guidance and approval of the Task Officer. The necessity of the sampling program is unquestionable; however, a $\pm$ 25% order of magnitude of error in estimating by engineering calculations may suffice for filling in data gaps.

Task 6.0: General Program Support

An information storage and retrieval system was developed and put into full operation in August, 1976. In the past year, Catalytic, Inc. has provided technical assistance to Beard Engineering, Inc. A visit was made to Baton Rouge, La. to discuss monitoring and sampling requirements for a FOX combined plant being designed for the Louisiana Municipal Power Commission, and a trip report was prepared detailing the results of the visit. A report was also prepared presenting the results of the Japanese trip, the sources of information and a brief description of the information obtained.

Status of Environmental Assessment Program on Residual Oil Utilization

A depiction of the methodology of functions and relationships in the environmental assessment process was given in reference EPA documents "IERL-RTP Environmental Assessment Guideline Document, First Edition" dated March, 1976, and the draft by R. F. Hangebrauck dated May 11, 1977, for Energy Assessment and Control Division Programs (Figure 1). The environmental assessment (EA) strategy is divided into several steps. The status of these steps for the residual oil utilization study follows:

Current Environmental and Process Technology Background--

Identification of current residual oil processes and their environmental backgrounds has included a study of process flowsheets, status and schedules; identification of possible emission sources within the process; projection of possible emissions by means of theoretical calculations and engineering consideration; listing of potential pollutants; collection of health/ecological effects, transformation/transport, and related information for potential pollutants. This information has been gathered, analyzed, and tabulated for the energy consumption, economical merit, and environmental acceptability. Most of the emission loadings to all media have been defined for comparison with CAFB and with any other new residual oil processes entering the commercial or demonstration stages; however, information concerning health, ecological effects and transformation/transport at ambient conditions has been delayed by other contractors.

Environmental Objectives Development--

Development of environmental objectives based ultimately on health and ecological effects of possible pollutants and expressing the goals in terms of acceptable emissions has severe built-in delays. Pollutants are prioritized based upon partially available effects. The goals depend upon health and ecological effects rather than the process. The cause of delays in this step is ascribable to the incompleted draft Multi-media Environmental Goals (MEG) charts that list approximately 200 substances. The MEG charts targeted for June, 1977, have been delayed considerably.

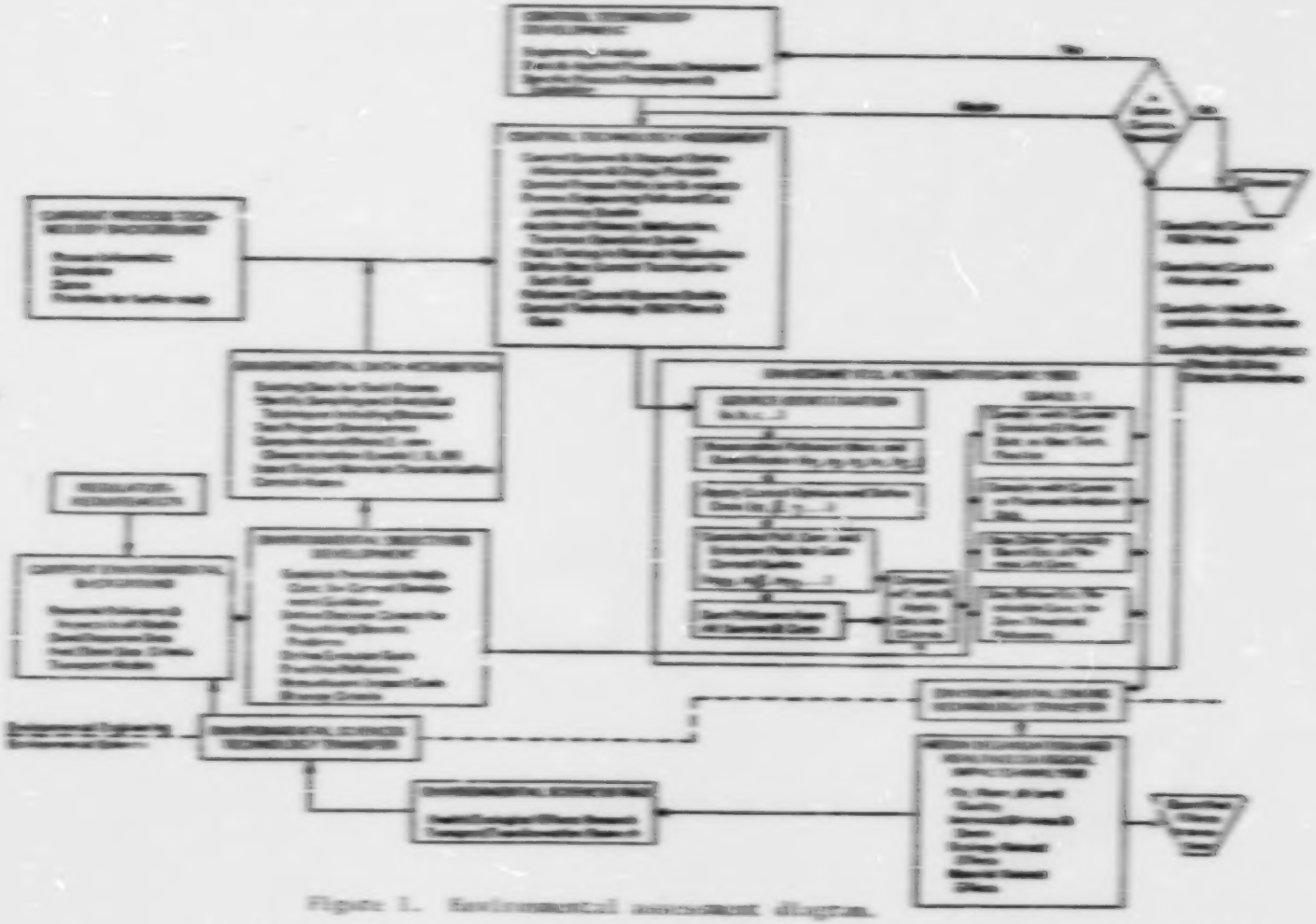

Figure 1. Instrumental account digram.

Environmental Data Acquisition--

Comprehensive analyses of emissions from existing commercial facilities require further sampling and analysis. A staged analytical approach will determine, in the most cost effective manner, which of the potential pollutants are being emitted and at what levels. All Level I sampling criteria was not completed during this first year of effort, but some preliminary guidelines will be followed for gathering data from some of the residual processes. The bioassay criteria and protocol need to be established this coming year.

Control Technology Assessment--

Assessment of available control technology, including identification of specific control technologies, evaluation of the cost of alternative degrees of control, and a preliminary assessment of the environmental impact of the control process have been completed. Best available technology was evaluated for Flue Gas Desulfurization (FGD), hydrodesulfurization (HDS) and partial oxidation (POX) combine cycle systems. The nitrogen oxide scrubbing or the flue gas denitrification is still in the developmental stages. This technology may be commercially applied in a few years for an economic and environmental assessment. It is possible, when sampling in Japan, that a residual oil-fired utility boiler may be available for our performance tests and analysis next year. The final disposal of HDS catalysts may be investigated at this same time.

Environmental Alternatives Analysis--

Analysis of environmental alternatives have been initiated for FGD, HDS and POX to identify the optimum combination of control devices for all pollutants and process streams considering the trade-offs between cost and degree of control. Using the Source Analysis Model (SAM)/IA - for Rapid Screening, the FGD, HDS and POX control options were applied to a residual oil-fired utility power plant (75 to 500MW). The SAM/IA technique is aimed at determining which option FGD, HDS or POX is most environmentally effective and at defining the problem pollutants in terms of relative degree of hazard. Best commercially available control technology will be defined using NSPS existing standards for liquid fossil fuel power plants.

SECTION 4

RESIDUAL OIL GASIFICATION PROCESS (POX)

DESCRIPTION OF PROCESS

Over 100 commercial Partial Oxidation Reactors are now in successful operation around the world. Over half of these are charging Residual Fuel Oil with many others on Crude Oil. Others operate on light oil, naphtha and natural gas.

At the present time, there is only one commercial unit in the Continental United States. This unit charges Residual Fuel Oil and produces hydrogen. Another unit is operating on mixed feeds in Puerto Rico, and a Lurgi unit is operating on naphtha in Hawaii. Three additional units are planned for completion in the near future.

Essentially, any residual fuel oil or lighter hydrocarbon can be charged. The residual fuel oil is partially oxidized to form a gaseous mixture of carbon monoxide (CO) and hydrogen (H_2) with a small amount of methane (CH_4). Either oxygen (O_2) or air ($O_2 + N_2$) can be used for the partial oxidation. Some carbon dioxide (CO_2) and carbon soot (C) are formed as by-products. When air is used, the nitrogen remains in the gas product. When oxygen is used, the peak temperatures are usually controlled by a dilutant such as steam or carbon dioxide. Carbon soot is produced as a result of incomplete combustion.

Residual fuel oil contains hydrocarbons and certain contaminants such as sulfur (S), nitrogen (N), ash, and various metals, which are mainly sodium (Na), vanadium (V) and nickel (Ni). The sodium is usually reduced to a sufficiently low level by crude oil desalting before the residue is fed to the reactor. Excessive sodium could damage the reactor lining. Some of the ash components, including vanadium and nickel compounds, along with some

hydrogen cyanide (HCN), ammonia (NH_3) and any formic acid (HCO_2H) formed, are removed from the product gas in a water scrubber, since they are either soluble or suspended in water. The carbon soot remains in suspension in the water and can be removed by naphtha extraction or other recovery methods. The soot may then be recycled to the reactor for further reaction. Some ash is removed from the reactor as friable slag during shutdown for inspection. The sulfur products are only slightly soluble in water and therefore remain in the product gas stream as hydrogen sulfide (H_2S), with some carbonyl sulfide (COS) and a trace of carbon disulfide (CS_2).

Several commercial processes are available for removal of up to 99+ percent of the H_2S from the product gas. Some processes selectively remove the H_2S, leaving much of the CO_2 in the gas. The CO_2 is desirable when using the gas as fuel to a gas turbine. By removal of much of the CO_2, using other absorbents, the product gas will have a higher Btu content.

The desulfurized product gas with essentially all the CO_2 removed will have a Btu value of 320 to 325 Btu/SCF,HHV when O_2 is used for the oxidation. By comparison, the product from air oxidation will have a Btu value of 120 to 125 Btu/SCF,HHV because of the nitrogen remaining in the gas. Because O_2 is more costly than air, the product gas from O_2 partial oxidation is more costly per MM Btu produced.

DESCRIPTION OF EQUIPMENT

Salt Removal. If residual fuel oil has been transported by ship, rail or truck, a chance of contamination by salt water always exists. The salt content should be reduced to 10 pounds or less per 1,000 barrels of oil in order to prevent damage to the reactor lining. Water washing, followed by electrostatic precipitators or centrifuges to remove the salt water, are usually adequate. Where high salt contents must be removed, several units in series may be required.

Feed Preheaters. All feed to the reactor should be preheated for maximum efficiency. This requires preheaters for the residual fuel oil and oxygen or air.

Reactor. In the reactor there are two zones - the combustion zone and reaction zone. The fuel oil and air or oxygen are intimately mixed in the

combustion zone where part of the oil is burned and part is cracked by the resulting high temperatures. In the reaction zone, the combustion products react with the cracked products to form the desired product gas. The combustion must be carefully controlled by limiting the oxygen, as excess combustion will increase the carbon dioxide produced, and insufficient combustion will produce excess carbon in the product gas. Carbon is a by-product of the reaction and may be recovered and recycled to the reactor as a suspension in the residual fuel oil feedstock. The design and installation of the reactor refractory liner, and the design of the burners, is critical for proper operation of the process.

Waste Heat Exchanger. Much of the efficiency of the gasification process depends upon recovering the maximum heat possible. The waste heat exchanger at the outlet of the reactor is used to recover much of this heat in the form of steam. Treated feedwater is charged to the exchanger and, because of the high temperatures at the reactor outlet, high pressure-saturated steam is generated.

In addition to the design of the waste heat exchanger for high temperature and pressure, special design must be used to allow the carbon by-product to pass through the exchanger without fouling. Such fouling would reduce the amount of steam produced, thus lowering the efficiency of the process. Treated feedwater preheating in an economizer exchanger is usually used to further cool the reactor product gas in order to recover more heat. Additional heat recovery may be obtained from the product gas after slurry separation and before gas scrubbing. (Figure 2)

Product Gas Wash. The product gas from the economizer is contacted by water in a spray vessel followed by a carbon slurry separator; most of the soot is removed here. The remaining soot is removed from the product gas in a scrubber. The water wash is designed to remove essentially all of the product gas contaminants that are soluble in water plus the carbon soot and certain ash compounds which remain suspended in the water. These contaminants are mainly carbon, ash, including vanadium and nickel compounds, hydrogen cyanide, ammonia and traces of formic acid. All of these contaminants are potential pollutants and should be handled accordingly. By treating the spent wash water, the hydrogen cyanide, formic acid and ammonia can be disposed of safely, leaving only the metals and ash.

Carbon Separation: The carbon soot may be separated from the water by several methods. One method involves using naphtha extraction of soot from water suspension followed by transfer to fuel oil. The naphtha is recovered by distillation from the naphtha/soot/fuel oil mixture. This produces a soot/feedstock slurry which can be recycled to the reactor for converting into additional product gas. Besides the soot being a potential pollutant, it also contains some ash, vanadium and nickel. (Figure 3)

Sulfur Removal: The product gas from the water scrubber still contains most of the sulfur compounds and carbon dioxide. Thus, it is necessary to pass the gas through a contactor containing an absorbent for removal of hydrogen sulfide. In addition to the hydrogen sulfide, which is the major sulfur component in the gas, there is also some carbonyl sulfide and traces of carbon disulfide. An absorbent should be chosen that will also remove as much as possible of these sulfur compounds. All of these sulfur compounds will normally form sulfur dioxide if the product gas is burned, and they should be considered as pollutants.

The carbon dioxide in the product gas is a dilutant. When the product gas is to be used as a fuel for gas turbines, the carbon dioxide has some beneficial effects and is normally left in the gas. Under these conditions, a selective H_2S absorbent is usually chosen that will absorb the CO_2 to a lesser extent. When a higher Btu content of the gas is desired, an absorbent is chosen that removes both the sulfur compounds and the carbon dioxide. (Figure 4)

Sulfur Recovery: Disposal of the hydrogen sulfide removed in desulfurization usually calls for the addition of a Claus unit. Hydrogen sulfide is charged to the Claus unit to produce sulfur. The effluent gas from this unit usually contains some residual sulfur dioxide and should be considered as a potential pollutant. However, further processing is available which will reduce the sulfur emission to very low levels such as a SCOT or IFP unit. (Figures 4 & 5)

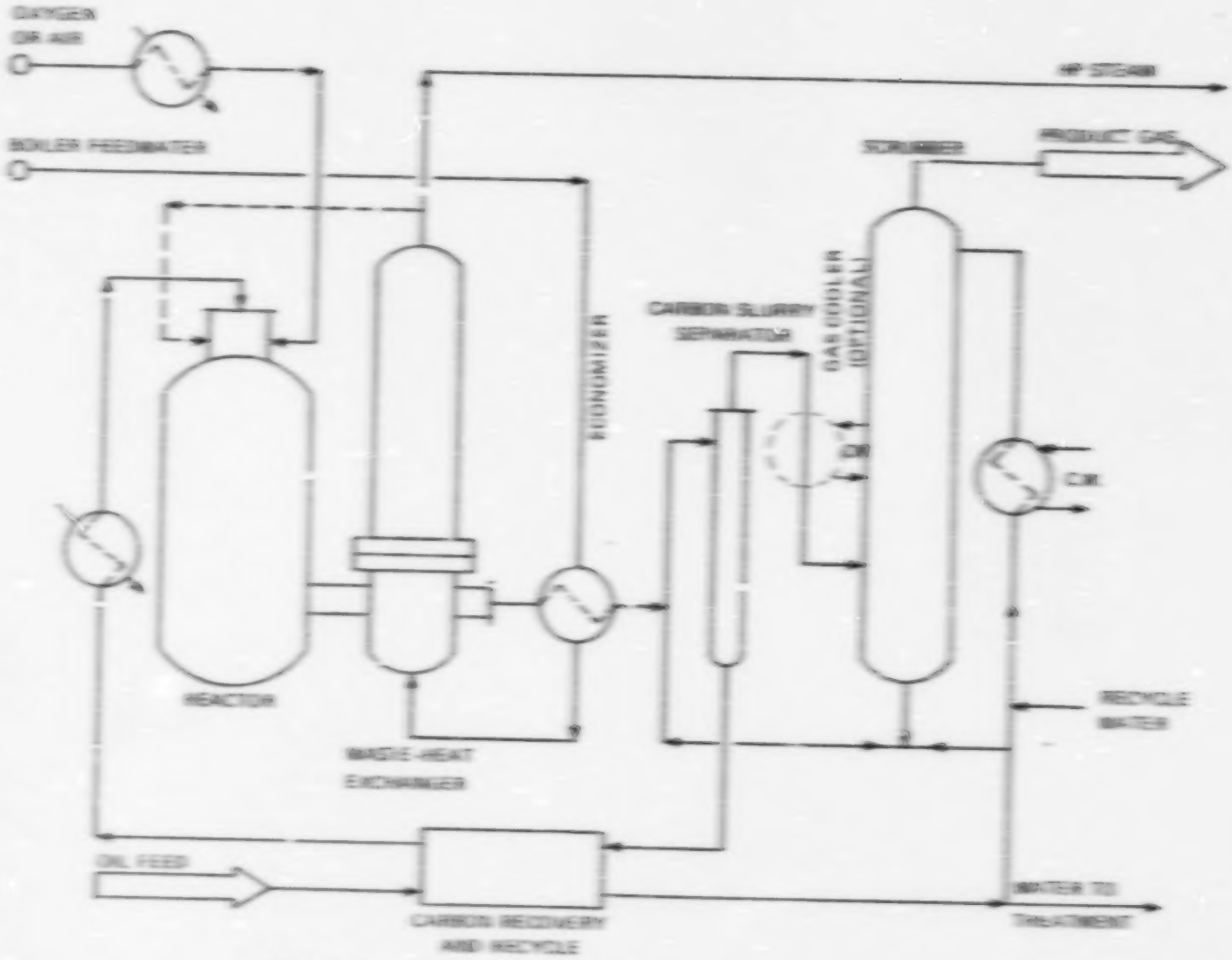

Figure 1. Shell Gasification Process

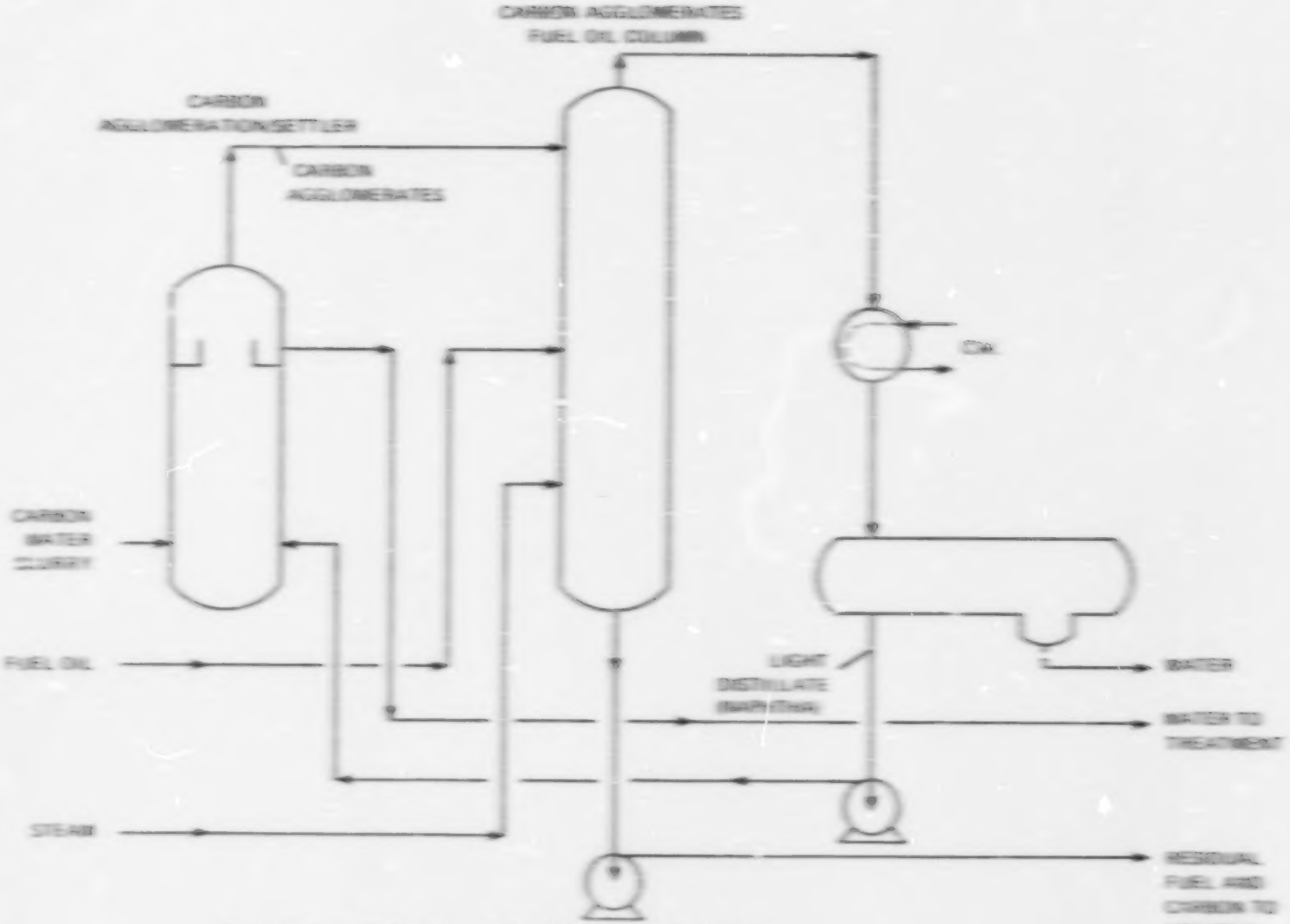

Figure 1. Shell Chasol Carbon Recovery System.

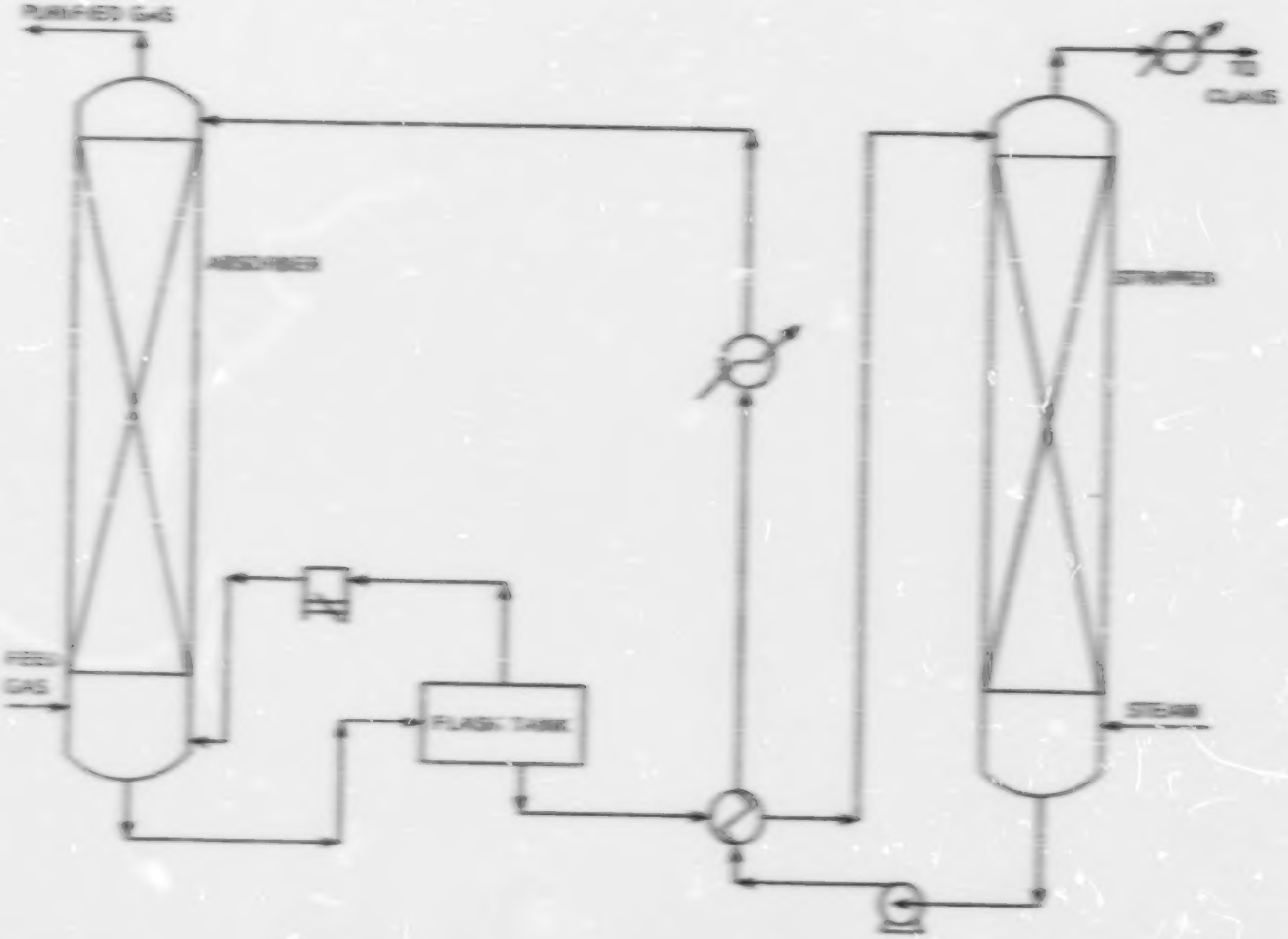

Figure 4. Selexol H_2S removal process.

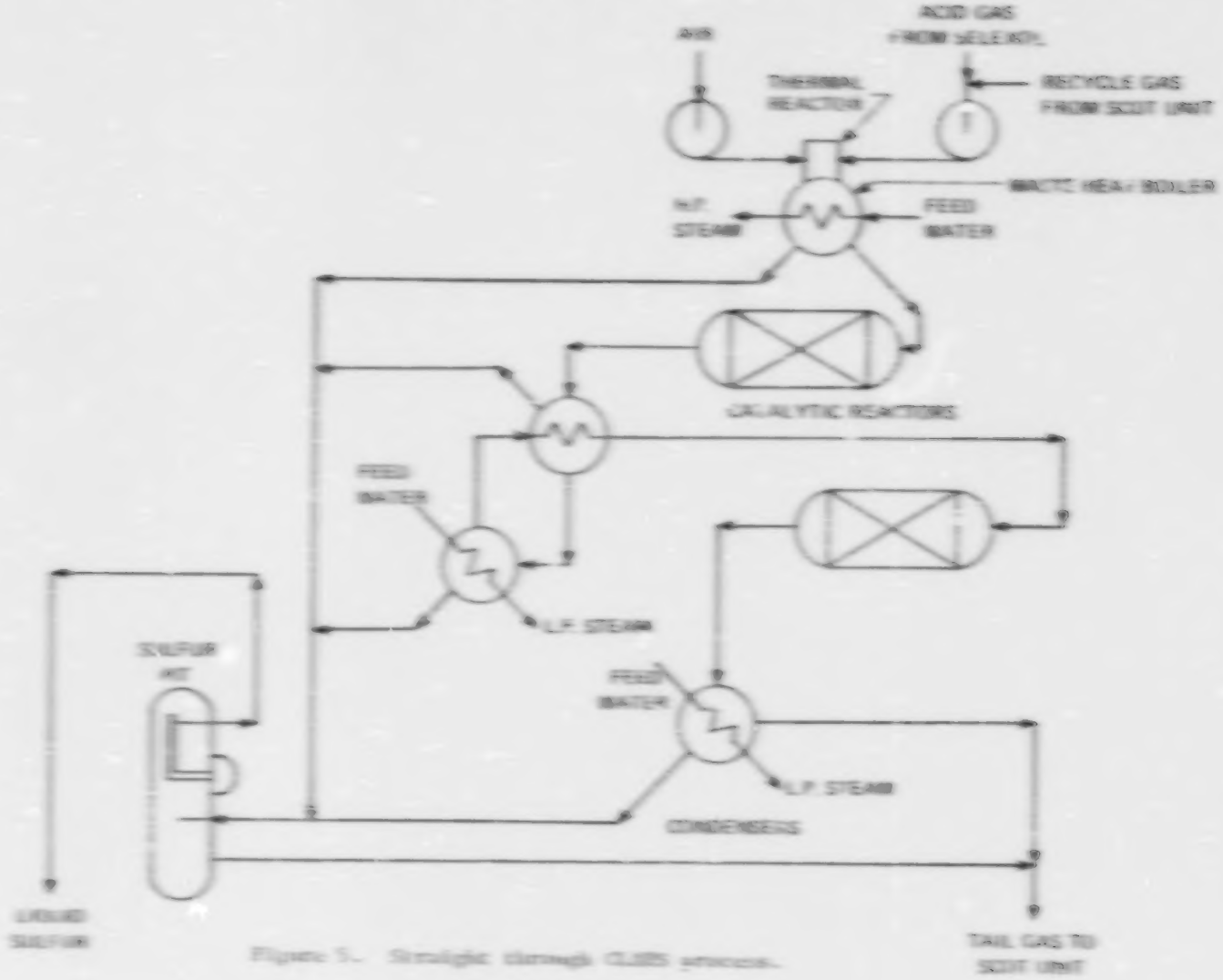

Figure 1. Straight through CLSS process.

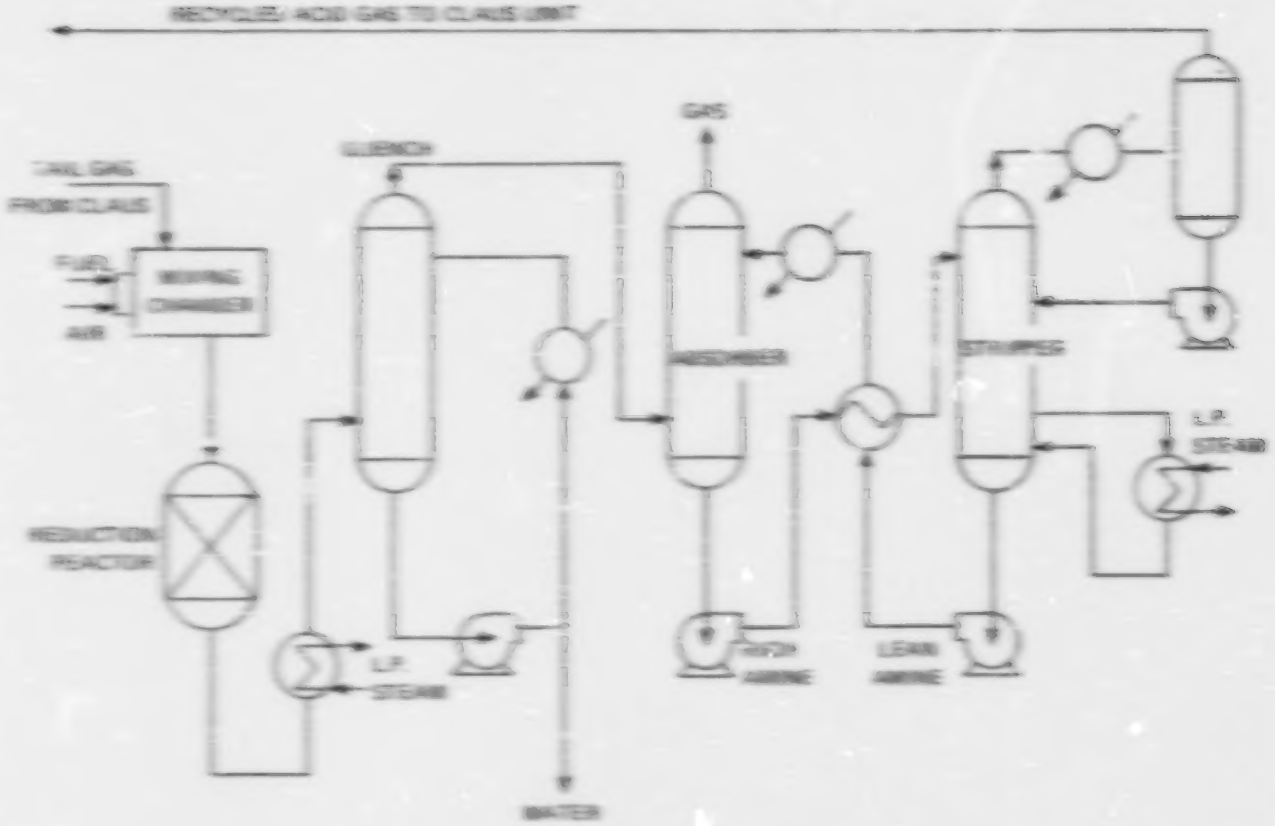

Figure 4. Shell Claus Off-Gas Treating (SCOT) process.

Figure 7 shows a typical residual oil gasification unit with steam generation. Streams are numbered, and a description of each stream follows. Steam heat can be used on the feed instead of fired heaters.

Figure 8 shows typical cleanup units with carbon separation and recycle, hydrogen sulfide removal in a Selexol unit, production of sulfur in a Claus unit, and cleanup of the Claus effluent gas in a SCOT unit.

Table 1 gives a description of each stream in the POX process plus the associated additional equipment for cleaning up the gas stream.

Table 2 is a summary of all of the significant potential pollutants from the process. They are listed beneath the streams in which it is possible for them to exist. Each stream should be analyzed on a commercial unit in order to determine the existence and emission level of each potential pollutant.

Table 3 shows typical feedstocks and products to a residual fuel oil gasifier, commonly called a partial oxidation unit (POX). These feeds and products are the basis for the numbers shown in the following tables.

Table 4 is a weight balance around a unit to produce a gas at the heat rate of 2.5×10^9 Btu/hr, higher heating value (HHV) or 2.35×10^9 Btu/hr, lower heating value (LHV).

Table 5 indicates the efficiency of the above unit. The first efficiency is through the oxidizer and heat recovery system which shows a 93 to 96% heat recovery range when compared to the heat content of the feed charged. The second efficiency shows 79.2% after all sulfur removal and cleanup equipment is considered.

Table 6 considers all of the potential pollutants which can be produced in the process and follows them through each piece of equipment, showing the possible level in each stream under normal operating conditions.

Table 7 is an estimate of the capital costs and operating costs of the above unit. It indicates that when charging a residual fuel oil to this size unit costing $10/bbl., a clean 118 Btu/(LHV) gas at 375 psig can be produced for approximately $3/MM Btu.

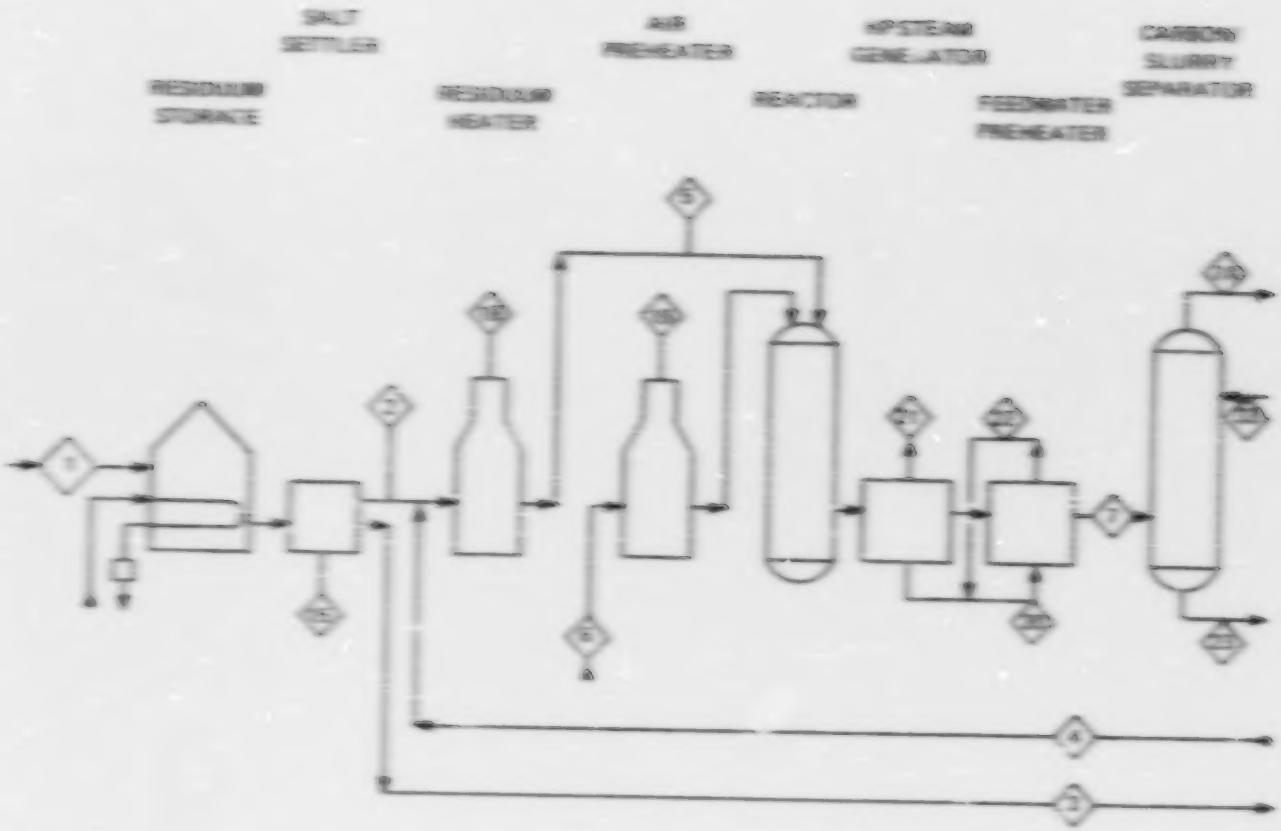

Figure 7. Typical residual oil gasification unit (POX).

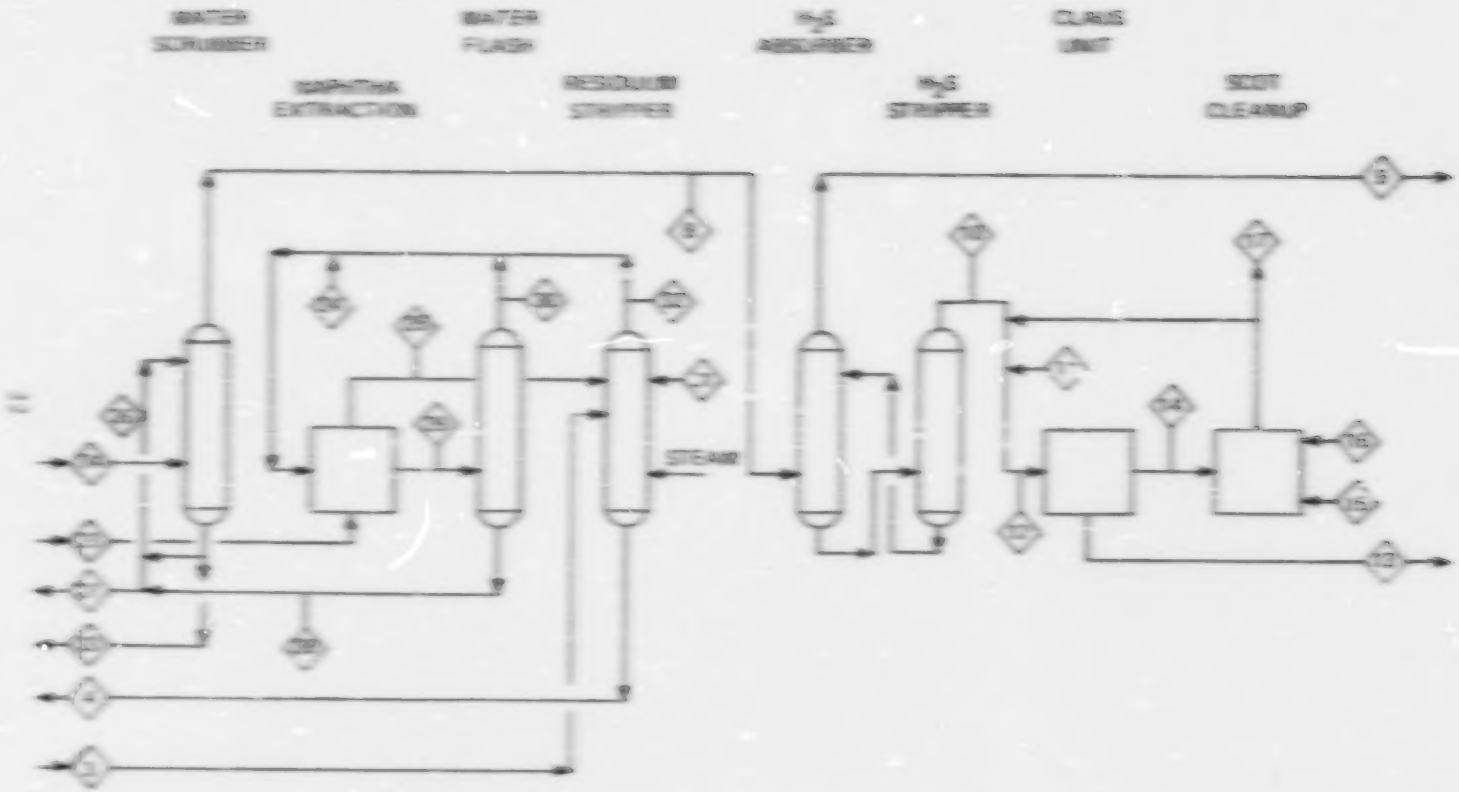

Figure 4. Typical gasification island unit for (IGCC).

TABLE 1. DESCRIPTION OF FLOW FROM FIGURES 6 AND 7

Stream No.	Stream Description
1	Residual Fuel Oil to Heated Storage
2	Residual Fuel Oil to Feed Preheater
3	Residual Fuel Oil to Carbon Recovery
4	Residual Fuel Oil Plus Carbon From Recovery
5	Residual Fuel Oil Plus Carbon From Feed Preheater
6	Process Oxidation Air to Feed Preheater
7	Cooled Process Gas to Water Wash
7A	Gas to Water Scrubber
8	Water Scrubbed Process Gas to Acid Gas Scrubber
9	Clean Process Gas Product
10	Hydrogen Sulfide Plus Carbon Dioxide to Claus Unit
11	Combustion Air to Claus Unit
12	Total to Claus Unit
13	Sulfur Product
14	Claus Effluent Gas to SCOT Unit
15	Combustion Air to SCOT Unit
16	Fuel Gas to SCOT Unit
17	SCOT Unit Stack Gas
18	Residual Oil Preheater Stack Gas
19	Stack Gas From Process Oxidation Air Preheater
20	Treated Feedwater to Preheater
21	High Pressure Steam
22	Preheated Feedwater
23	Carbon and Water From Carbon/Slurry Separator
24	Naphtha Makeup to Naphtha Extraction
25	Naphtha and Carbon From Naphtha Extraction
26	Water Makeup to Water Scrubber
27	Waste Water
28	Recycle Water to Water Scrubber
29	Water Plus Entrained Naphtha to Water Flash
30	Stripped Naphtha From Water Flash
31	Naphtha Reflux
32	Naphtha Stripped From Residuum/Carbon Mixture Water to Carbon Slurry Separator

TABLE 2. SUMMARY OF POTENTIAL POLLUTANTS

Carbon By-product

- Vanadium
- Nickel
- Other Ash Components

Effluent Wash Water

- Soluble and Suspended Ash Components
- Carbon (Minor)
- Vanadium
- Nickel
- Hydrogen Cyanide (minor)
- Formic Acid (trace)
- Ammonia (minor)

Product Gas

- Carbon (trace)
- Carbon Monoxide
- Hydrogen Sulfide (minor)
- Hydrogen Cyanide (trace)

Burned Product Gas

- Sulfur Dioxide
- Carbon Monoxide
- Particulate Matter (minor)

TABLE 3 . TYPICAL FEED AND PRODUCTS

Feedstocks

Oil Feedstock

Kuwait 1050^{0}F+ Residue

Gravity, ^{0}API	5.6
S.G. 60/60^{0}F	1.032
Lb/Bbl	361.5
Composition, % wt.	
Carbon	83.72
Hydrogen	9.68
Sulfur	5.55
Nitrogen	.30
Oxygen	.50
Ash	.05
	100.00
Viscosity, SSF	
310^{0}F	1,300
275^{0}F	160
Metals, ppm wt.	
Nickel	30
Vanadium	130

Naphtha For Soot Recovery

Gravity, ^{0}API	60
S.G. 60/60^{0}F	0.739
Lb/Bbl	258.3
Composition, % wt.	
Carbon	85.19
Hydrogen	14.81
	100.00

Final Gas Product

Final Product Gas

Estimated Composition, % Volume	
Hydrogen	14.3
Carbon Monoxide	23.7
Carbon Dioxide	0.02
Water	0.28
Methane	0.26
Nitrogen	60.65
Argon	0.76
Hydrogen Sulfide + Carbonyl Sulfide	—300ppm
Total	100.00
Average Molecular Weight	24.33
Higher Heating Value, BTU/SCF	123.3
Lower Heating Value, BTU/SCF	118.0

TABLE 4. WEIGHT BALANCE FOR PROCESS (AIR OXIDANT)

Stream No.		Input M lb./hr.	Output M lb./hr.
1	Residuum	205.9	
24	Naphtha	1.8	
6	Air to Gasifier	1,226.5	
		1,434.2	
9	Clean Product Gas		1,278.0
13	Sulfur		11.0
			1,289.0
17	Losses - CO_2 and H_2O		145.2

TABLE 5. ENERGY BALANCE FOR PROCESS (AIR OXIDANT)

Basis: $2,350 \times 10^6$ Btu/hr. Net Heating Value Final Product Gas

Stream No.		Million Btu/hr.	%	Million Btu/hr.	%
1	Net Heating Value of Residuum Feed	3,407.2			
24	Net Heating Value of Naphtha Feed	35.5			
		3,442.7	100%		
9	Net Heating Value of Clean Product Gas			2,350	68.3
21-22	Enthalpy of Surplus Steam Generated			953	27.7
	Efficiency Before Sulfur Removal			3,303	96.0 *
	Heat Required for Sulfur Removal			618	18.0
13	Heating Value of Sulfur Produced			52	1.5
	Heating Value of Net Surplus Steam and Gas After Sulfur Removal			2,737	79.5

* maximum value indicated, however, may be as low as 93%

TABLE 6. POTENTIAL POLLUTANT STREAMS

The list of streams below does not include the steam boiler and cooling tower blow downs, as these are common to many other units. Also, it does not include the water effluent from the salt settler on the residual oil feed.

Stream No.	Description	Potential Pollutant	#/hr.
9	Product Gas 1,278,000#/hr. 830,000 SCFH	H_2S	300
		COS	83
		CO	302,900
		HCN	Trace
		Particulate	Trace
17	SCOT Stack Gas	SO_2	40
		NO	
		Particulate	43
18	Residuum Heater Stack 45,100#/hr. 11,600 SCFM	SO_2	43
		NO	160
		Particulate	14
19	Air Preheater Stack 360,000#/hr. 92 500 SCFM	SO_2	330
		NO	1,270
		Particulate	115
27	Wash Water Effluent 42,300#/hr.	Ash	100
		Va	28
		Ni	6
		HCN	Trace
		Phenol	Trace
11	Sulfur 11,000#/hr.	H_2S	Trace

TABLE 7. TOTAL COSTS OF PRODUCING 2.35 x 10^9 BTU/HR (LHV) OF PRODUCT GAS

Capital Costs	Millions of 1977 $
Gasification Unit	43.45
Desulfurization	19.23
Sour Water Stripping	.11
Sulfur Recovery	7.48
Waste Water Treatment	4.09
Booster Compressor	9.15
Cooling Tower	2.30
Other Expenses	1.79
	85.62

Operating Costs

Variable	Units	Costs, ¢/Units	¢/10⁶ Btu
Residual Fuel	bbl	1000	235.0
Naphtha	bbl	1200	2.4
			237.4
Steam			
1350 psia	lb	0.453	(151.0)
1275 psia, 925°F	lb	0.570	127.7
65 psia	lb	0.402	1.0
Cooling Water	MGal	2.0	3.8
Electricity	KWH	3.9	1.8
Boiler Feed Water	gal	.08	1.1
			221.0

Fixed	¢/10⁶ Btu
Operating Labor	3.0
Direct Overhead	1.2
Operating Materials	0.4
Total Operating Expense	4.6
Maintenance Labor	3.3
Maintenance Material	3.3
Direct Overhead	2.0
Total Maintenance Expense	9.0
Indirect Overhead	4.4
Taxes, Ins., Royalty, etc.	1.8
	6.2
Total Operating Cost	241.8
Capital Charge for 55 E.P.	54.2
Fuel Gas Mfg. Cost	296.0

SECTION 5

DIRECT HYDRODESULFURIZATION

The rapid growth of energy consumption in heavily industrialized countries, such as Japan and the United States, has created a large demand for heavy fuel oils. The increase in consumption created a rise in ambient sulfur dioxide concentrations. To reduce the environmental impact of the combustion of these fuels, sulfur-in-fuel regulations were adopted. In Japan, for instance, utilities are required to burn from as low as 0.1% sulfur by weight to no greater than about 1.0% sulfur.

One method of producing these low sulfur fuel oils (LSFO) is direct hydrodesulfurization of reduced atmospheric crudes.

Since 1968, reduced crude direct hydrodesulfurization technology has been applied to produce LSFO from Middle East atmospheric residues. There are at this time 11 commercial direct RDS units operating with a combined production capacity of 459,000 barrels per day of low sulfur fuel oil (LSFO). Ten of the 11 units are in Japan. Information about the location, licensee, licensor and capacity of each of the plants appears in Table 8.

PROCESS DESCRIPTION

The direct hydrodesulfurization process consists of 7 interconnected unit operations:

1. Storage and Pretreatment
2. Reaction Section
3. Separation Section
4. Recycle Gas Purification
5. Sulfur Recovery

TABLE 8. COMMERCIAL DIRECT HYDRODESULFURIZATION FACILITIES

Licensee	Plant Location	Licensor	Plant Capacity (BPD)
AMINOL	Kuwait	UOP	35,000
Asia Oil	Yokohama, Japan	UOP	30,000
Idemitsu Kosan	Aichi, Japan	Gulf	50,000
	Chiba, Japan	UOP	40,000
	Hyogo, Japan	Gulf	40,000
Kashima Oil	Kashima, Japan	UOP	45,000
Maruzen Oil	Chiba, Japan	Union Oil	60,000
Mitsubishi Oil	Mizushima, Japan	Gulf	45,000
Nippon Mining Co.	Mizushima, Japan	Gulf	31,000
Okinawa S. S.	Okinawa, Japan	Gulf	38,000
Seibu Oil	Omoda, Japan	Shell	45,000

6. Tail Gas Treatment

7. Fractionation Section

As shown in Figure 9, atmospheric reduced crude from the storage and pretreatment section passes into the reactor after being combined with makeup hydrogen and recycle gas. In the reactor, the sulfur in the reduced crude combines with the hydrogen to form hydrogen sulfide (H_2S). The reactor effluent enters a series of flash vessels which separate the stream into liquid, recycle-gas and sour fuel gas fractions. The liquid streams pass to a distillation column for fractionation into low sulfur fuel oil (LSFO), middle distillate, naphtha, and sour fuel gas. The recycle gas goes to an amine scrubber where the H_2S is removed. It is necessary to remove the H_2S, since its presence in the hydrogen-rich recycle gas would reduce the desulfurization rate. This purified recycle gas is either used as quench gas to moderate the reactor's temperature or mixed with the feed and make-up hydrogen. The rich amine passes to an amine regenerator for separation of the recycle amine and hydrogen sulfide.

The H_2S rich off-gas stream from the amine regenerator passes to a Claus unit for recovery of the sulfur. The Claus feed stream may contain 95-99% H_2S, of which about 97% is converted into molten sulfur. The unconverted H_2S exits the unit in the form of sulfur dioxide (SO_2). Since the SO_2 concentrations in the Claus tail-gas are generally significantly higher than national or local standards, additional control, in the form of a tail-gas treater (TGT), is required.

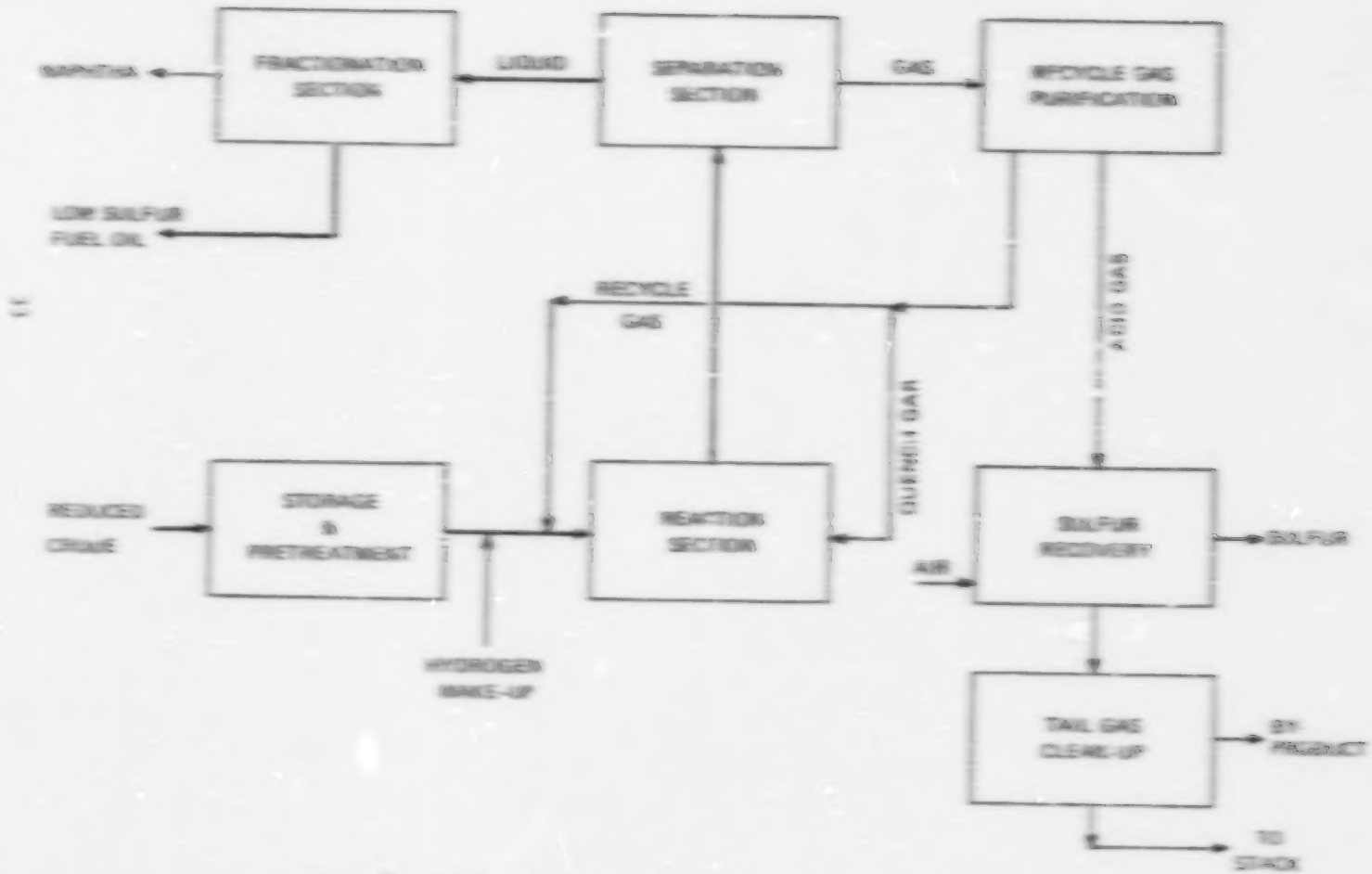

Figure 9. Direct hydrodesulfurization unit operations.

MATERIAL BALANCE AROUND HDS UNIT

Typically, the HDS system has two input streams and eight output streams.

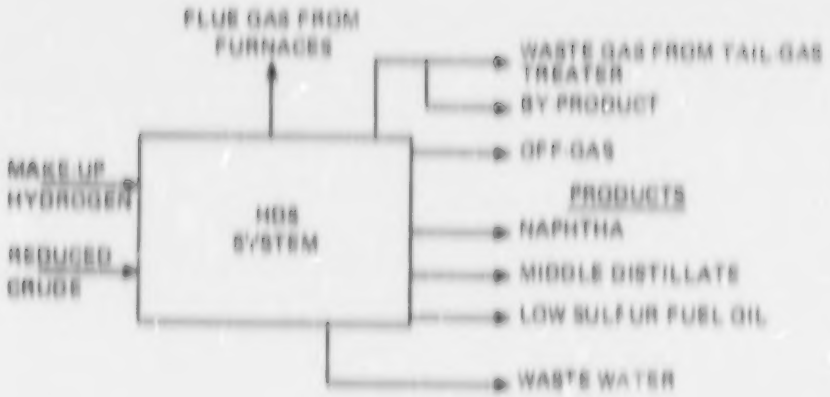

Figure 10. HDS entering and exiting streams.

A representative material balance appears in Figure 11. The data is for the Shell HDS unit at the Seibu Oil Refinery in Yamaguchi, Japan. Similar diagrams are being prepared for the Gulf and Universal Oil Products (UOP) licensed units visited.

HDS EMISSIONS

In the previous section, there are three streams leaving the HDS system which interface directly with the environment:

1. Flue gas from furnaces
2. Waste gas from tail-gas treater
3. Waste water

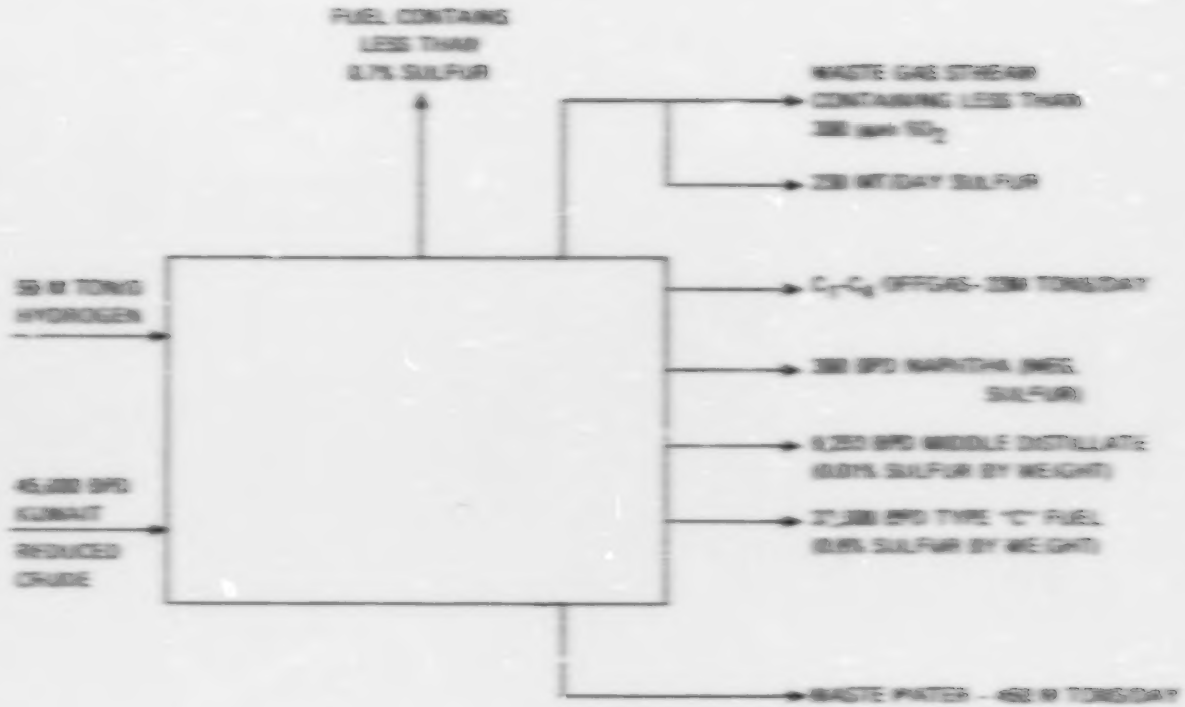

Figure 11. Material balance for Shell IRS *vs.*
45,000 barrel-per-day design basis

Sour Off-Gas

The C_1-C_4 off-gas stream is not emitted directly to the atmosphere. Instead, the stream is combined with other refinery "sour" fuel gas streams and sent to an amine scrubber for removal of the H_2S. The scrubbed gas then goes to a fuel gas pool for use throughout the refinery. Because of the higher make-up hydrogen requirements in the Gulf Type IV process (produces 0.1-0.3% sulfur fuel oil), the sour fuel gas from the HDS unit passes to a hydrogen recovery unit.

The selection of furnace fuels, tail-gas treatment and waste water separation and treatment are dependent upon:

1. National and local air and water pollution emission standards.
2. Specific design and operating requirements of refinery
3. Feed and product requirements
4. Economics

Waste Water

Water is introduced into the HDS unit for two purposes:

1. As wash water to the reactor effluent coolers to remove ammonium hydrosulfide (NH_4HS)
2. As a condensed stripping stream

About 90% of the total sour water is from the wash with the remaining 10% being condensed steam. The combined stream is fed into a sour water stripper for separation of the liquid and gaseous streams. The combined feed typically has between 1.0-2.5 weight % H_2S and 0.5-1.0 weight % ammonia (NH_3). The waste water from the stripper contains approximately 5ppm by weight H_2S and 50ppm by weight NH_3. The stripped hydrogen sulfide and ammonia are piped to the sulfur recovery unit where they are combined with H_2S rich amine regenator off-gas. At the Idemitsu Kosan refinery in Hyogo Prefecture, the sour water passes to a Chevron waste water treatment (WWT) unit. This unit converts the sour water into three streams:

1. High-purity H_2S which is fed into the SRU

2. Pure saleable ammonia

3. Recycle water which is fed to crude oil desalter

Flue Gas From Furnaces

Various arrangements of heaters are used to preheat the reduced crude feed, make-up hydrogen, recycle gas and fractionator feed. During the Japanese trip, we found heaters fired by low sulfur fuel oil, fuel gas and a combination of these fuels. A limiting factor in the selection of heater fuel is the allowable emission standards. As an example, the SO_2 emissions standards in Yamaguchi Prefecture require the sulfur content of the furnace fuel be less than 0.5% by weight. In operation, the furnaces are fired by a combination of 70% oil and 30% refinery fuel gas. Since the gas contains virtually no sulfur, 0.7% sulfur oil can be used and the emission standards will still be met.

Tail Gas Treatment

A variety of tail gas treatment methods have been used to reduce the sulfur dioxide emission from the Claus units to environmentally acceptable levels. The process selection is based on consideration of items such as the desired degree of control, capital and operating costs, by-product credits and maintenance costs. Table 9 lists the tail-gas treatment techniques for the seven refineries visited. Only one unit, the thoroughbred 101 scrubber at the Nippon's Mizushima refinery, produces a saleable by-product. The SCOT units, although most expensive from an operating standpoint, result in the lowest SO_2 concentration (20-100ppm by volume).

PROCESS ECONOMICS

Present estimates for the desulfurization of reduced crude range from $2.00 to $4.00 per barrel. The cost depends on items such as hydrogen cost, size of plant, raw material costs, desired depth of desulfurization and the cost of money.

Data obtained on Japanese units is being analyzed, with the ultimate objective of determining the range of desulfurization for the actual operating units. Total capital costs were obtained for all seven plants; however, problems have been encountered in establishing an equal basis. In some cases, the

TABLE 9. TAIL-GAS TREATMENT OF COMMERCIAL UNITS

Refiner	Plant Location	Tail-Gas Treatment
Asia Oil	Yokohama	
Idemitsu Kosan	Aichi	Shell Claus off-gas treater (SCOT)
	Hyogo	Institut Francais de Petrole (IFP) tail-gas treater followed by incineration
Kashima Oil	Kashima	Shell Claus off-gas treater (SCOT)
Mitsubishi Oil	Mizushima	Institut Francais de Petrole (IFP) tail-gas treater followed by caustic scrubber
Nippon Mining Co.	Mizushima	Chiyoda thoroughbred 101 flue gas scrubber
Seibu Oil	Onoda	Shell Claus off-gas treater (SCOT)

cost included the sulfur recovery and tail-gas treater, while in other cases, the cost was not included. This is further complicated by the capital costs being for the year the unit was constructed. The year constructed varies from 1970 for the Kashima Oil unit to 1976 for the Seibu Oil facility.

Operating costs in the form of utilities, chemicals, catalyst and manpower present less of a problem. The data we acquired during the trip are in the form of quantities consumed, not cost. Appropriate cost factors will be applied to convert quantities into dollar-per-barrel costs.

SECTION 6

FLUE GAS DESULFURIZATION (FGD)

This study presents the results of a preliminary environmental assessment of the Flue Gas Desulfurization (FGD) process attached to a residual oil-fired boiler. All waste streams contributing to air, water and solid waste pollutants were evaluated in terms of emission rates. The FGD control technology assessment involved SO_2 removal efficiencies of burning high sulfur (2.5%) residual oil and evaluation of process control capabilities. The FGD process performance was also evaluated on the effective removal of particulates that carry the bulk of the trace elements and toxic substances. The reliability of the FGD process was considered under varying boiler loads, firing rates of residual oil and fuel contaminant content. The effects of transient conditions of start-up, shutdown and upset operating conditions on emission control were considered.

Some grab samples were taken for Preliminary I orientation and for the compilation of a partial emissions inventory of the residual oil-fired boiler in electric utility power plant. In addition to the environmental and control technology assessment, an economic evaluation of the FGD process relative to alternative residual oil utilization techniques is presented. Finally, recommendations are made for further environmental assessment procedures and for the control technology research and development to be carried out.

DESCRIPTION OF PROCESS

Although the most advanced flue gas desulfurization (FGD) processes are generally of the "throwaway" type which produce an unusable mixture of sulfur compounds, development work is also in progress on a number of "regenerable" processes which can ultimately produce either elemental sulfur or sulfuric acid as a by-product. Elemental sulfur is normally preferred because it is a non-corrosive solid which is easily handled, stored, and shipped.

Evaluations of all waste streams from the FGD systems and a tabulation of process emissions are included. These data were derived from engineering estimates, Dr. Ando, Pedco Surveys, and from various plant field sampling and laboratory analysis programs. Emission rates determined for the various utility power plants were then used to predict pollutant loadings for the FGD systems. These results are compared with legal requirements, quantifiable health, and ecological effects.

TYPES OF PROCESSES

This section describes the categories of the various Japanese plants listed in Table 10. The development of commercial FGD processes is listed in Table 11 by year demonstrated and by classification of operation.

Non-Slurry Processes

Sodium Solution Scrubbing - SO_2 Regeneration and Reduction to Sulfur--

Stack gas is washed with water in a venturi scrubber for removal of particulates and then washed in a spray scrubber with a recirculating solution of sodium salts in water for SO_2 removal. Makeup sodium carbonate is added to cover handling and oxidation losses of sodium sulfite to sulfate. Sodium sulfate crystals are purged from the system, dried, and sold. Water is evaporated from the scrubbing solution using a single-effect evaporator to crystallize and thermally decompose sodium bisulfite, driving off concentrated SO_2. The resulting sodium sulfite is recycled to the scrubber and the SO_2 is reacted with methane for reduction to elemental sulfur. The regeneration and reduction areas are designed as a cyclic absorption-desorption process for removing sulfur dioxide from waste gases and producing a concentrated sulfur dioxide gas for feed to a contact sulfuric acid plant or to a Claus sulfur plant.

Ammonia Process--

Flue gas is passed through a scrubbing tower and SO_2 is absorbed by an aqueous stream of ammonium hydroxide, bisulfite, and sulfite. Makeup ammonia is injected into the flue gas ahead of the scrubber. The scrubber effluent is filtered to remove sludge and then aerated to oxidize the ammonium sulfite to ammonium sulfate. The ammonium sulfate is crystallized in an evaporator and then centrifuged and dried (Figure 12).

Aluminum Sulfate Process--

Flue gas, after the acid mist has been removed, is sent to an absorption tower where SO_2 is absorbed by a basic aluminum sulfate solution. The enriched solution goes to a regenerator and SO_2 is stripped off by steam heating. The SO_2 stream is dried and returned to the sulfuric acid plant. A side stream of enriched solution is reacted with calcium carbonate to prevent buildup of SO_3 in the absorbent. The calcium sulfate is removed by filtration (Figure 13).

Slurry Processes

Limestone Slurry Scrubbing--

Stack gas is washed with a recirculating slurry (pH of 5.8-6.4) of limestone and reacted calcium salts in water, using a two-stage (venturi and mobile bed) scrubber system for particulate and SO_2 removal (Figure 14). Limestone feed is ground wet prior to addition to the scrubber effluent hold tank. Calcium sulfite and sulfate salts are withdrawn to a disposal area for discard. Reheat of stack gas to 175°F is provided.

Lime Slurry Scrubbing--

Stack gas is washed with a recirculating slurry (pH of 6.0-8.0) of calcined limestone (lime) and reacted calcium salts in water using two stages of venturi scrubbing. Lime is purchased from a nearby calcination operation, slaked, and added to both circulation streams. Calcium sulfite and sulfate are withdrawn to a disposal area for discard. Reheat of stack gas to 175°F is provided.

Magnesia Slurry Scrubbing - Regeneration to H_2SO_4--

Stack gas is washed using two separate stages of venturi scrubbing--the first utilizing water for removal of particulates, and the second utilizing a recirculating slurry (pH of 7.5-8.5) of magnesia (MgO) and reacted magnesium - sulfur salts in water for removal of SO_2. Makeup magnesia is slaked and and added to cover only handling losses, since the sulfates formed are reduced during regeneration. Slurry from the SO_2 scrubber is dewatered, dried, calcined, and recycled during which concentrated SO_2 is evolved to a contact sulfuric acid plant producing 98% acid.

TABLE 10. MAJOR WET-TYPE FLUE GAS DESULFURIZATION PROCESSES

	Categories	Absorbent	By-Product	Process Licensors
I.	Non-Slurry (Double Alkali)	Dil. Sulfuric Acid	Gypsum	Chiyoda
		Sodium Sulfite	Gypsum	Showa-Denko
				Kureha-Kawasaki
		Ammonium Hydroxide	$(NH_4)_2SO_4$	Showa-Denko
		Aluminum Sulfate	Gypsum	Dowa Mining
		Sodium Sulfite	SO_2 or Sulfur H_2SO_4	Wellman-Lord
II.	Slurry	Lime or Limestone	Gypsum	Mitsubishi H.I., Hitachi, etc.
			Calcium Sulfite (Throw-away)	Chemico
		Magnesium Oxide	H_2SO_4 or SO_2	Chemico

TABLE II. DEVELOPMENT OF COMMERCIAL FGD PROCESSES

Scrubbing Process	Year Demonstrated	Classification/ Operating Principles
1. Limestone/Sludge (CaO, $CaCO_3$) Absorbent	1968-71	Throwaway processes/wet absorption in scrubber by slurry; insoluble sulfites and sulfates disposed of as waste
2. Lime/Sludge ($Ca(OH)_2$) Absorbent	1971-72	Same as above
3. Magox-Sulfur (MgO) Absorbent	1972-73	Regenerative process/wet absorption in scrubber by magnesium oxide slurry magnesium oxide regeneration by calcining, SO_2 by-product sulfur
4. Catalyst Oxidation Acid (dilute H_2SO_4 with sodium salt absorbents)	1972-73	Regenerative process/catalytic oxidation by V_2O_5 catalyst into sulfuric acid
5. Sodium/Sulfur (Na_2SO_3, $NaOH$, Na_2CO_3) Absorbent	1973-74	Regenerative process/sodium base scrubbing with sulfite to produce bisulfite regeneration in evaporator-crystallizer; bleed stream purge of sulfate solution
6. Double Alkali/Sludge Na_2SO_3 + $CaCO_3$ or $Ca(OH)_2$ $(NH_4)_2SO_4$ + $CaCO_3$ $Al_2(SO_4)_3$ + $CaCO_3$, Sodium Acetate	1973-74	Throwaway process/wet absorption in scrubber; reaction products precipitation and removed from recycle stream
7. Ammonia/Sulfur or Fertilizer (ammonium salts) absorbent	1974-75	Regenerative process/ammonia base scrubbing with wet Claus recovery of sulfur or fertilizer application

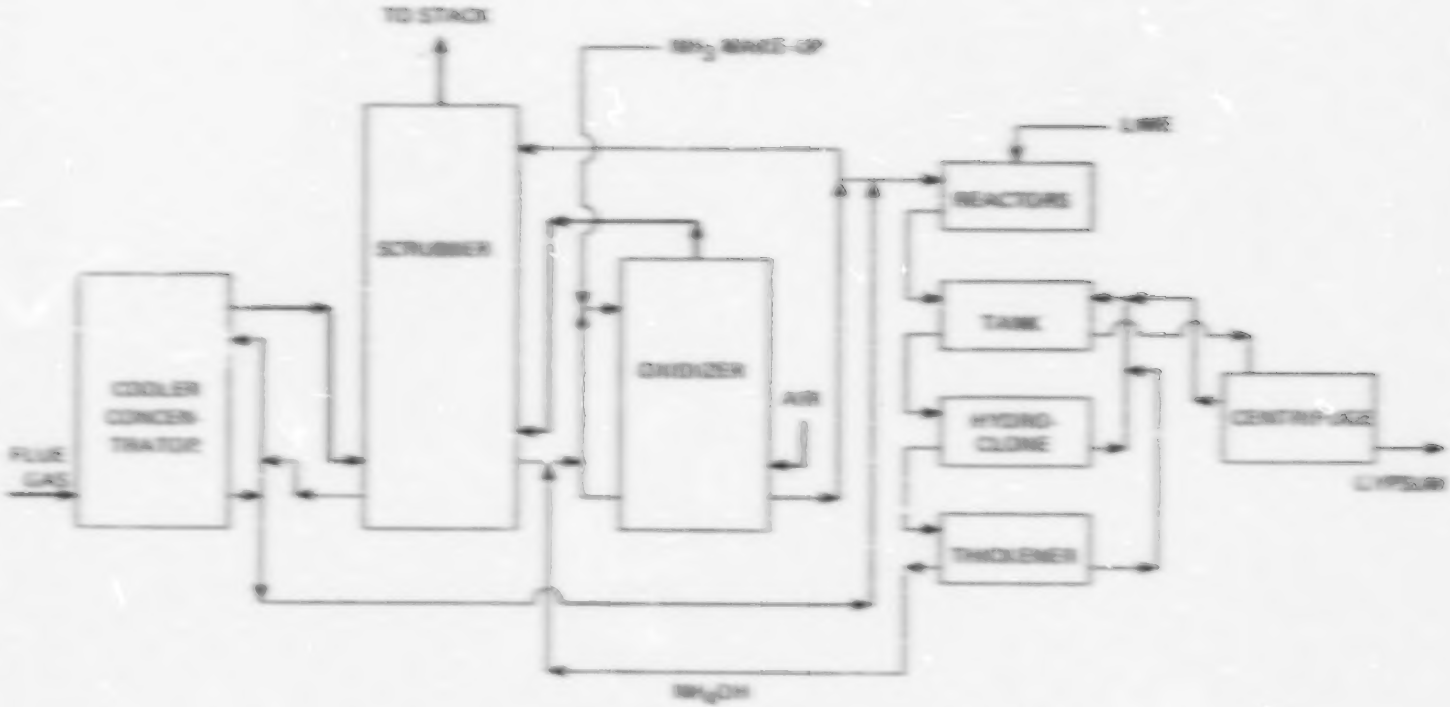

Figure 12. Double alkali process - [illegible]

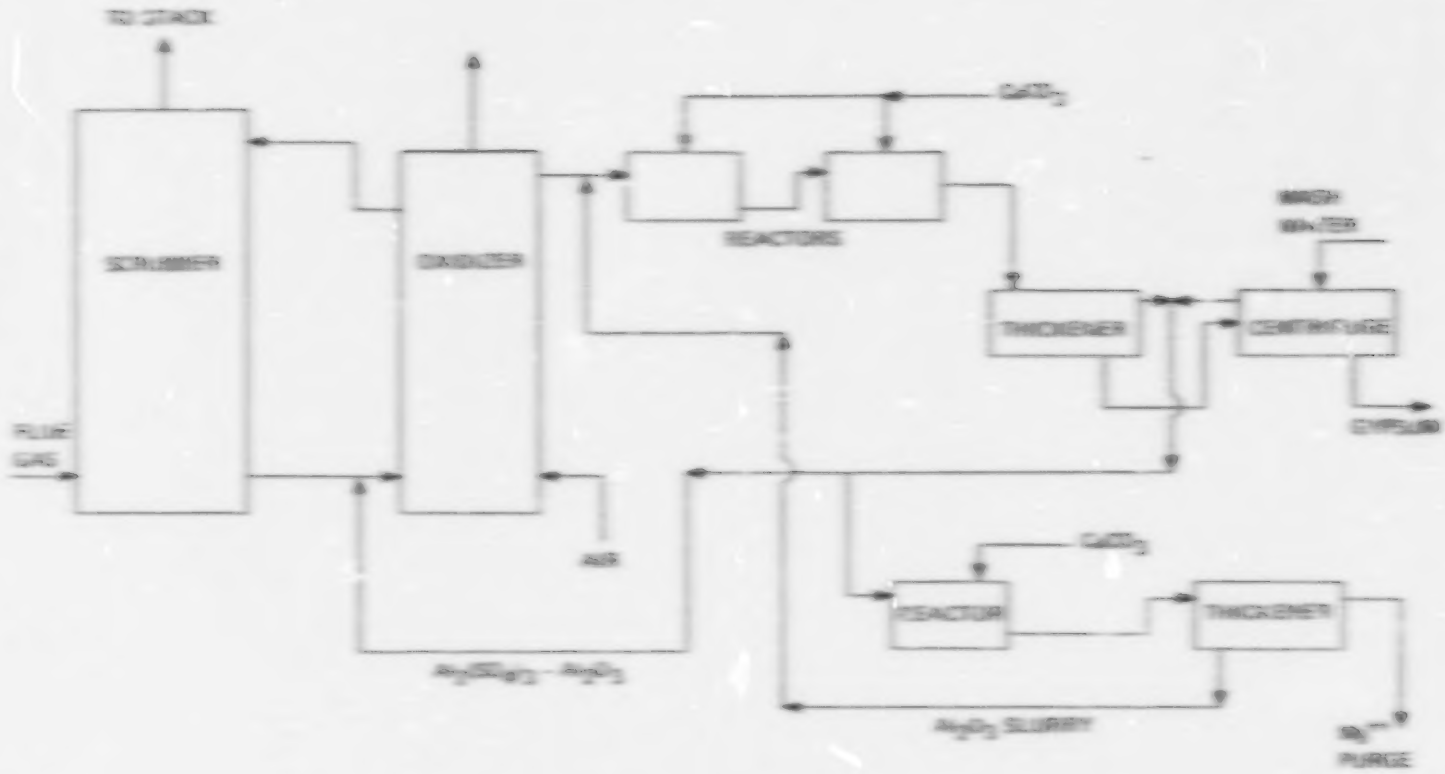
TO STACK
SCRUBBER
OXIDIZER
REACTORS
THICKENER
CENTRIFUGE
FLUE GAS
AIR
REACTOR
THICKENER
PURGE

Figure 11. [illegible]

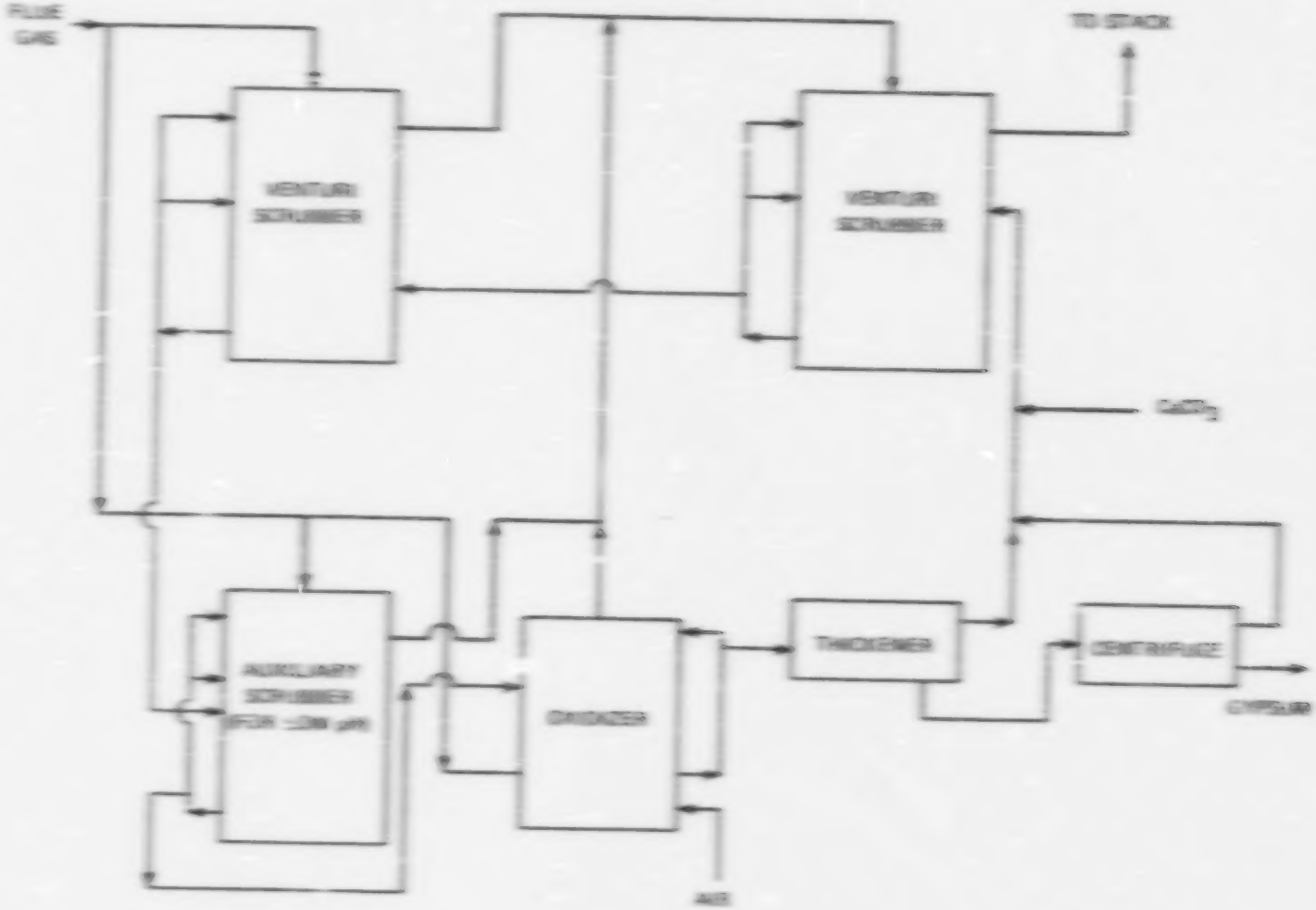

Figure 5. Limestone slurry scrubbing throwaway process.

POLLUTANTS

Important Pollutants in Stack Gas to FGD Units

1. Particulates
2. Sulfur oxides (SO_x)
3. Nitrogen oxides (NO_x)
4. Hydrocarbons (HC)
5. Carbon monoxide (CO)
6. Trace elements (8) elements)
7. Benzene soluble organics (BSO)*
8. Particulate polycyclic organic matter

   (PPOM) Benzo(a)pyrenes (BaP)
9. Polyhalogenated hydrocarbons (PHH)

Emission Sources in Terms of Unit Operations

Particulate emission rates vary with the type of fuel, as well as with boiler design and operating factors. Opacity and particulate matter are increased as the fuel ash content increases. Correct air-to-fuel ratios help minimize particulate emissions. Either an excess or lack of air restricts organic matter from being oxidized in the boiler. Oil-fired units require proper oil preheat temperatures to minimize emissions.

Essentially all sulfur in the fuel is oxidized to SO_2, and one to five percent of the SO_2 is oxidized to SO_3 during combustion. About 95 percent of the sulfur is emitted to the FGD, the remainder reacting with the ash.

The impact of the combustion of fuel oil on the concentrations of trace elements in aerosols has been shown to be dependent on the concentration of ash in the oil being burned in the boiler and also the firing rate.

Particulate emissions resulting from the combustion of fuel oil are dominated by sub-micron particles which contain most of the mass of many elements. The residence time of those particles in the atmosphere will be longer

than some other fuels.

Atmospheric Emissions--

From the FGD processes, these emissions are either particulate emissions or by-products of the scrubber chemical reactions. Particulate emissions result from the residual fuel oil ash content.

The Federal emission standards (NSPS) are:

Particulate	0.1 Lbs/10^6Btu or 0.13 GR/SCFD
SO_2	0.8 Lbs/10^6Btu or 330ppm
NO_x	0.3 Lbs/10^6Btu or 227ppm

The Massachusetts State regulations are:

	% Removal Efficiency
SO_2 = 61.3ppm(v)	93.6%
= 271.9 Lbs/hr	
= 0.201 Lbs/10^6Btu	
Particulate = 0.044 GR/SCFD	65.4%
= 130 Lbs/hr	
= 0.095 Lbs/10^6Btu	

These standards were applied to a magnesium oxide FGD test run. The oil analysis used in the magnesium oxide FGD process (Figure 15) was composed of: (1) sulfur, 1.89 to 2.15%; (2) ash, 0.07 to 0.10%; and (3) carbon varied from 84.39 to 84.79%. The 150MW power plant emitted 3771 to 4317 lbs. per hour SO_2 as input to the FGD scrubber whose outlet was 200 to 294 lbs. per hour or a SO_2 removal efficiency varying from 89.3 to 92.7%. The nitrogen oxides were not analysed.

The particulate input to the FGD scrubber ranged from 151 to 399 lbs. per hour of by-products of combustion and oxidation for a removal efficiency of 43 to 70%. Removal efficiency of particulates of less than 1 micron varied from 33 to 65%. This shows a typical inefficiency of most venturi-type scrubbers. The health effects on living tissue of these submicron particles is well documented. The spectrographic analysis indicated the following concentrations

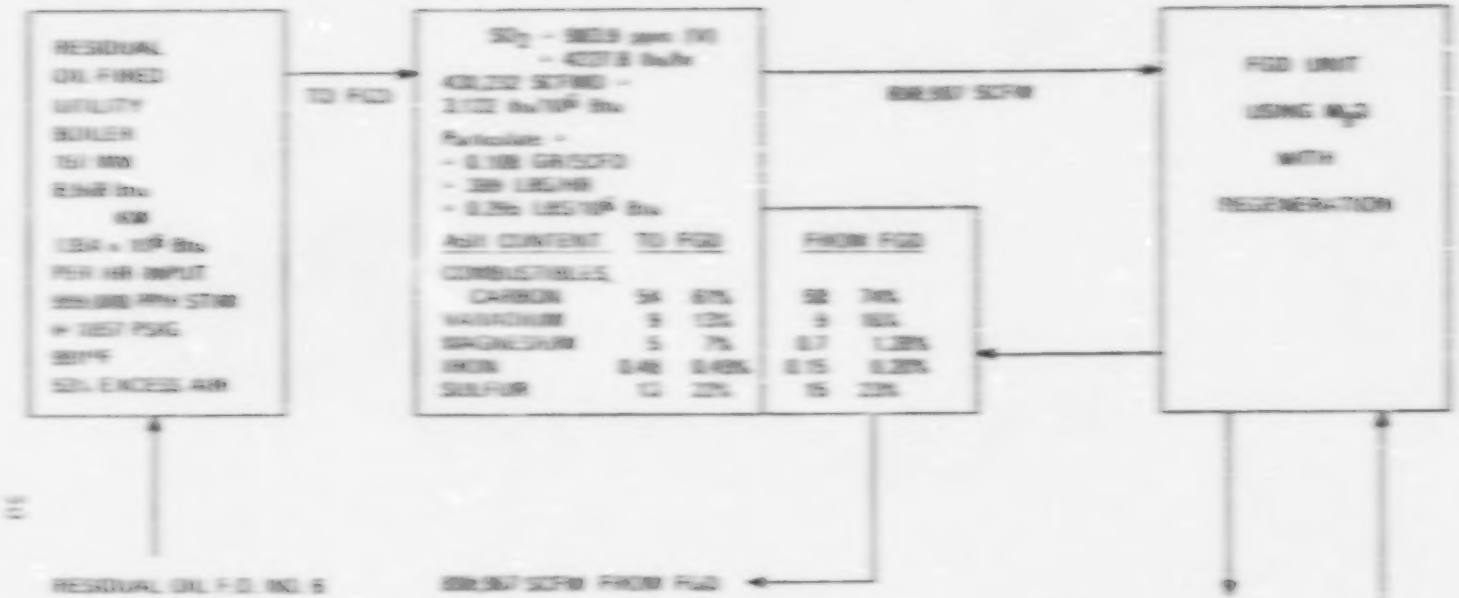

Figure 15. Test run on FGD unit using $Mg(OH)_2$

of toxic elements in the FGD source emissions: vanadium varied from 980 to 1320ppm; sodium, 5100ppm; zinc, 680ppm; aluminum, 200ppm; and Co-12ppm, Ni-8ppm, Cu-17ppm, B-5ppm, and several others were below 1ppm in the residual oil as fired.

Solid Wastes Emissions--

In the regenerated MgO process, the vanadium input in scrubber varied from 0.43 to 1.55% and the nickel varied from 0.08 to 0.174% over a 9 month period.

The greatest fugitive dust losses for this project occurred at the regeneration plant where 0.3 tons per day were scalped off the calciner product as large lumps before the pulverization process. Future system design will provide for the reclaiming of these losses. In addition, 1.3 tons per day were lost from the neutralizer overflow. In subsequent designs, this large loss can be recovered for recycle by separation of solids in the neutralizer overflow. The material balance calculation showed a loss over the entire power plant operation of 0.37 tons per operation day. This loss represents about 3.3% of the total MgO make-up rate.

	MgO (Dry Basis)
Loss to Stack	0.13 tons per day
Scrubber Overflow	0.14 tons per day
Miscellaneous	0.10 tons per day
Total	0.37 tons per day

Waste Water and Solid Wastes--

These have been discussed in other sections of this report in detail with reference to Table 12.

Commercial Unit Emissions

Limestone Slurry Process--

A considerable quantity of $CaSO_3/CaSO_4$ solid waste is generated, approaching as much as 4 times the weight of the sulfur removed. Wastes discharged to settling ponds are reported to have poor settling properties. This may lead to difficulty when reclaiming the land for future use. Potential runoff from the ponding site could lead to additional water pollution problems as shown in Table 12 indicating high make-up water and high waste-water ratios. Another

TABLE 12. WASTEWATER FROM FGD PLANTS

Rank	Process	MW	Inlet SO_2 (ppm)	Water (T/hr.)	Makeup Water Ratio %	Waste-Water Ratio %
1.	Babcock-Hitachi	900	1,900	9.0	20	10
2.	Wellman-IHI	220	1,000	3.0	--	1/
3.	Mitsubishi (IHI)	750	1,480	14.0	37	19
4.	Showa Denko	150	1,400	3.9	45	23
5.	Chubu-IHI	85	1,300	3.5	82	41
6.	Chiyoda	350	1,540	34.0	84	68
7.	Chemico Mitsui*	150	2,830	40.6	39	21

*STACK DRAINAGE ANALYSIS

	6/13/73	7/17/73	7/18/73
Load	145 MW	145 MW	145 MW
pH	4.1	4.3	3.3
SO_4 (As $MgSO_4$)	13.3%	7.0%	5.3%
Ni	0.01%	0.006%	0.003%
R_2O_3*	0.12%	0.18%	0.22%

* $R_2O_3 = Fe_2O_3 + Al_2O_3$

disadvantage of the Limestone Slurry process is low operating reliability from slurry plugging of scrubber internals. Also, reheat and high pressure drop cause an increase in already high energy consumption as indicated in Table 13. One advantage of the process, besides being the oldest and most economical process, is the elimination of electrostatic precipitators by a high particulate removal efficiency of 63% as shown in Table 14.

Magnesia Slurry Process--

This process has the following advantages: (1) capability of achieving above 90% SO_2 removal efficiency; (2) minimal waste water or solid disposal problems; (3) excellent flexibility for by-product switching from sulfuric acid to elemental sulfur; and (4) simultaneous SO_2 and NO_x removal efficiency (Table 14).

Double Alkali Process--

A simpler and more reliable process than the lime/limestone, it has the same pollution problems common to throwaway processes in having high waste water and waste solids to dispose as depicted in Table 12 (Chiyoda process). It is more reliable than the lime process because a clear solution is used in the scrubber with less possibility of buildup of scale.

Weak Acid Process--

The advantages of this process are: (1) simplicity and reliability of the various unit operations involving clear absorbent solution; (2) capability of achieving high SO_2 removal efficiency (95% or better, Table 13, item 7); (3) ability to produce non-polluting elemental sulfur or high strength sulfuric acid; (4) high reliability when provided with high surge capacity before and after the absorber during highly variable boiler load changes. The disadvantages are: high power requirements and thiosulfate blood-off stream pollution unless oxidation is complete.

The Acetic Acid Double Alkali Process--

This process has a high degree of SO_2 absorption efficiency of less than 1ppm SO_2 in the exit gas when the inlet gas enters at 1500-1700ppm. This unusually high SO_2 removal efficiency is obtained by the use of perforated trays with high L/G values and the high SO_2 affinity of sodium acetate recirculating on each tray. A typical block diagram is shown in Figure 16.

TABLE 19. COMPARISON OF DESIGN AND OPERATING PARAMETERS VERSUS PERFORMANCE

No.	Identification: Developer	Design Parameters: Capacity 1,000 m^3/hr.	Absorbent Precipitant Stoichiometry	Type of Absorber	Operating Parameters: Slurry or Solution pH	Conc. %	Energy Related Parameters: L/G Liters Per m^3	Pressure Drop * mm H_2O	Process Performance Efficiencies: SO_2 ppm In	Out	% Removal of SO_2
1	IHI Mitsubishi-Jamco	1,200[d]	CaO LC	CP[a]	6.6	10	10	200	1,600	30	98
2	Mitsui	870	$CaCO_3$ 95-?	Venturi	6	5	10-15	200	1,500	750	90
3	Babcock-Hitachi	1,450[c]	$CaCO_3$ 1.1-1.2	JP[b]	6.1	20	10	650	1,500	60	96
4	Kureha-Kawasaki	1,350[d]	Na_2SO_3 $CaCO_3$	CP[a]	6.2	20	10	150	1,870	5	99.5
5	Showa Denko	500[c]	Na_2SO_3 $CaCO_3$	Cone	6.0	25	1-2	Scrubber duty 250	1,400	40	97
6	Nippon Kokan	250	$(NH_4)_2SO_4$ CaO	Screen	6	30	2	250	700	30	96
7	Chiyoda	1,650	411 $CaSO_4$ $2H_2O$	Tellerette	1	2-4	55-60		1,600	60	96
8	Kureha	100	$(NH_4)_2SO_4$ CaO	Tellerette	4	10	4-10	100	1,500	80	95

[illegible]

TABLE 13 (continued)

Identification		Design Parameters			Operating Parameters		Energy Related Parameters		Process Performance Efficiencies		
			Absorbent Precipitant Stoichiometry		Slurry or solution						
No.	Developer	Capacity 1,000 Nm^3/hr		Type of Absorber	pH	Conc. %	L/G Liters Per Nm^3	Pressure Drop * $mm\ H_2O$	SO_2 ppm In	Out	% Removal of SO_2
9	Dowa	150	$Al_2(SO_4)_3$, $CaCO_3$	Tellerette	4	10	1[c]	100	400	20	97
10	Kureha	5	$Ch.(NH_4)_2SO_4$, $CaCO_3$	pp[b]	5.5	20	7-8[d]	200	1,400	1-5	99.6

a - Grid packed
b - Perforated plate
c - Four scrubbers in parallel
d - Two scrubbers in parallel
e - For tail gas at 25°C. L/G 6-10 for flue gas
f - Dissolved in $CaCl_2$ solution
g - Including limestone scrubbing
* - Including cooler, absorber and mist eliminator

In Table 14, the acid mist (SO_3) ppm(v) values are consistently high and above U.S.A. EPA standards. Japan does not distinguish between SO_3 and SO_2 emission separately, but they are both combined under the SO_x regulations in Japan. There is no specific incentive to control SO_3 by the Japanese utility industry. However, there are processes for mist elimination by designers and operators not listed in Table 14 that do accomplish good acid mist control within the U.S.A. EPA standards of 20ppm, such as: Mitsubishi Heavy Industries, Fugi Kosui, IHI, Babcock-Hitachi and Mitsui Miike. The amount of sulfuric acid mist generated is directly dependent upon the amount of excess air used in the combustion of residual oil. The submicron acid mist particles escape readily past most absorption towers when a specific mist elimination device is not designed into the FGD system.

TABLE 14. ENVIRONMENTAL POLLUTANT CONTROL CAPABILITIES OF REGIONAL OIL-FIRED BOILER FLUE GAS CLEANING PROCESSES

Type of Process	Size of FGD Unit (MW)	NO_x (ppm)	% of NSPS	Outlet SO_2 ppm	SO_2 Removal Eff. (%)	Acid Mist SO_3 ppm(v)	% of NSPS	NO_x Reductions ppm(v)	Total Particulates NSPS	Total Particulates grains/m^3
1. (a) H_2SO_4	100	430,000	11%	10-40	96-98	50			50%	0.035
2. (b) Sodium Sulfite	90	240,500	9%	50	95-98	65			67%	0.046
3. (b) Aluminum Sulfate	100	250,000	26%	10-30	95-99	42				—
4. (b) $Mg(OH)_2$ + $CaCO_3$	85	230,000	24%	130	95-96	65	68%	200	83%	0.058
5. Limestone	500	(960,000)	8%	44	96-97	—			47%	0.033
U.S.A. EPA Standard for New Source Performance (#2)-Diesel Boilers (77) for 1,000 MW	—	—	100%	550*	—	20	100%	1170	100%	.148

* $\frac{(0.80\ lbs.\ SO_2)}{1 \times 10^6\ Btu}$ # $\frac{(0.30\ lbs.\ NO_2)}{1 \times 10^6\ Btu}$ @ $\frac{(0.05\ grains)}{SCF}$

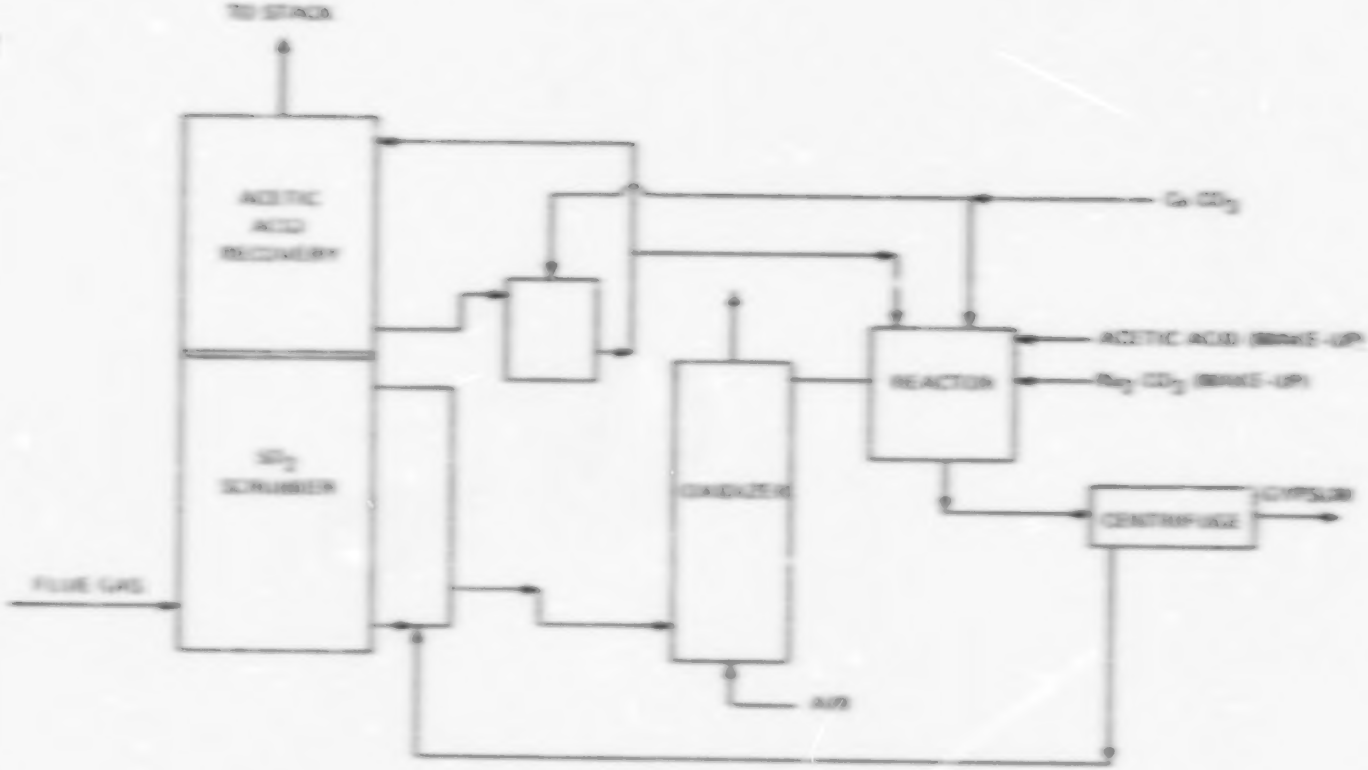

Figure 1b. Double alkali process – sodium acetate-dimethoxy

Projection of Control Efficiency for Important Pollutants

Most projections of control efficiency of important pollutants can be based upon Japan's experience with FGD systems applied to oil-fired utility boilers. The Japanese historical trends in SO_2 reduction could become an example for the U.S.A. for the future.

For a new plant with a capacity of 500MW in the Tokyo and Osaka areas, the sulfur content of oil charged to a boiler must be below 0.3% even with a 200m stack. As a result of these regulations, the importation of low-sulfur fuels, hydrodesulfurization of heavy oil, and flue gas desulfurization, the ambient SO_2 concentration has decreased as shown below.

Figure 17 shows the ambient SO_2 reduction in Japan over the last 12 years, during which FGD and other processes have demonstrated emissions control.

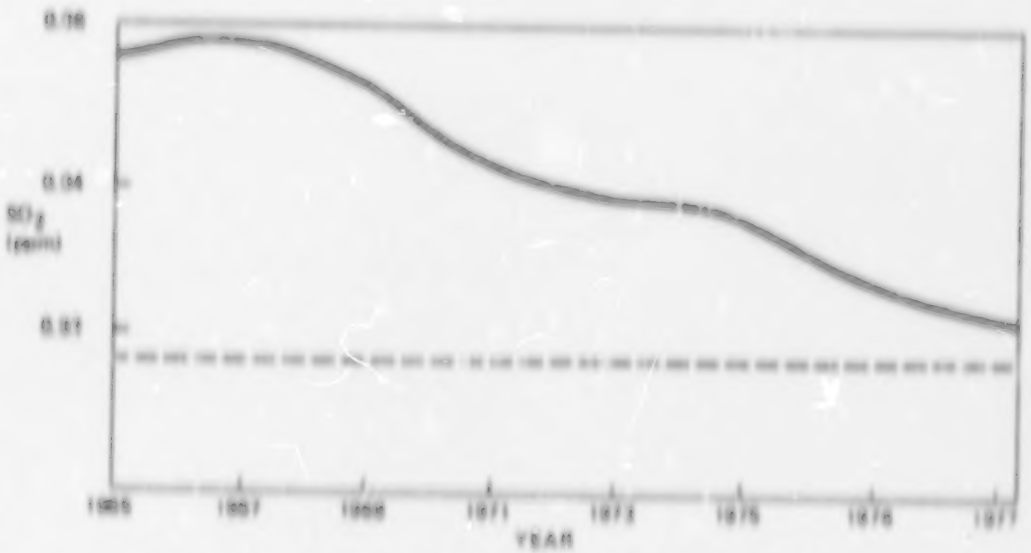

Figure 17. Sulfur dioxide reduction trends in Japan.

The ambient standard for SO_x concentration has been changed from 0.05ppm (yearly average) to 0.04ppm (daily average). As a result of the new standard, the hourly average should not exceed 0.1ppm and the daily average should not exceed 0.04ppm. The standard is more stringent in Japan than in the U.S.A. and West Germany.

TABLE 15. AMBIENT AIR QUALITY STANDARDS

(Daily or yearly average converted into ppm by vol. at plant boundary)

	SO_x		NO_2	
	Daily	Yearly	Daily	Yearly
Japan	0.04	(0.016)	0.02	(0.008)
U.S.A.		0.03	(0.13)	0.05
West Germany		0.05		0.05

The ambient air quality standard for NO_2 in Japan was set forth in 1973 at 0.02ppm in daily average, the most stringent figure in the world (Table 15). The present yearly average of NO_2 concentration ranges from 0.02 to 0.03ppm, and the daily average often reaches 0.04-0.07ppm in many cities.

The SO_x emission standard for stationary sources was first set up in 1973 and revised in 1975. Table 16 shows the standard for boilers larger than 100,000 Nm^3/hr. Similar figures have been assigned to smaller boilers between 10,000 and 100,000 Nm^3/hr since 1975. The standard is also more stringent in Japan than in the U.S.A. and other countries.

The main reason the acid mist values are high and above U.S. EPA standards is because Japan does not specify SO_3 emission loading standards; therefore, no tight control is indicated by Japanese industries. New standards for particulates by Japan when enforced may solve this problem. The non-restrictive particulates regulations or standards allow the Japanese industry an escape clause on SO_3. The expensive acid mist, SO_3 mist eliminators, are costly to operate because the high pressure drop requires extra fan horsepower and power costs. Another solution is to have high exit stack entrance free board space prior to

TABLE 16. NO_x EMISSION STANDARD (ppm)

Fuel	For new boilers		For existing boilers	
	1973	1975	1973	1975
Gas	130	100	170	130
Oil	180	150	230	230
Coal	480	460	750	750

Combustion modification and improvement of burners has been carried out to meet the standard. The ambient air quality standard, however, cannot be attained even with more stringent emission standards. More stringent regulations to restrict total quantity of NO_x emissions from stationary sources need to be applied. The new regulations in Japan require the construction of many flue gas denitrification plants which remove more than 80% of NO_x.

Estimated Capital and Operating Costs

Among the various FGD processes, the sodium scrubbing process with by-product of sodium sulfite is the simplest and most economical. The second lowest cost control technique on SO_2 is the throwaway wet-lime process, but this requires a large disposal pond. A plant based on the wet lime-gypsum process costs about 25% more than the throwaway process but does not require a waste pond.

Examples of plant cost within battery limits are shown in Table 17. The cost went up sharply during the middle of 1975 because of inflation and the active demand for FGD plants.

In Japan, a wet lime-gypsum process plant (200-300MW) now costs approximately $55-60/kW in battery limits, while a plant based on the indirect lime/limestone process costs 5-30% more. A plant using sulfuric acid by-product processes costs 30-70% more than the wet lime-gypsum process.

TABLE 17: PLANT COST IN BATTERY LIMITS ($1 = ¥300)
(The cost nearly tripled in late 1973 and has decreased considerably since late 1975.)

Process	Absorbent	By-product	Capacity (TPD)	Plant Cost 1973 ($ Dollars)	($/kW)	Year Completed
Wellman-IMX	Na_2SO_3	H_2SO_4	70	2.6	37	1971
Sumitomo S.B.	Carbon	H_2SO_4	55	2.8	51	1971
Chemico-Mitsui	$Ca(OH)_2$	Sludge	138	3.3	24	1972
Hitachi-Tokyo E.P.	Carbon	Gypsum	150	5.6	39	1972
Wellman-IMX	Na_2SO_3	H_2SO_4	220	7.0	32	1973
Shell	CuO	SO_2	40	3.3	83	1973
Chubu-IMX	$CaCO_3$	Gypsum	89	2.6	29	1973
Chemico-Mitsui	MgO	SO_2	180	13	72	1974
Mitsui-Chemico	$CaCO_3$	Gypsum	250	16	64	1974
Mitsubishi (MHI)	CaO	Gypsum	188	11.5	61	1974
Kureha-Kawasaki	Na_2SO_3	Gypsum	430	32	71	1973
Chiyoda	H_2SO_4	Gypsum	150	26	74	1973
Babcock-Hitachi	$CaCO_3$	Gypsum	300	33	70	1973
Wellman-IMX	Na_2SO_3	H_2SO_4	160	20	133	1973

Examples of FGD costs to remove 80-95% of SO_2 by the wet lime-gypsum process are shown in Table 18. The cost is about $15-17/kW or 3.0-3.9 mil/kWhr for different sized plants at 7 years depreciation and at 7,000 hours yearly operation.

TABLE 18. FGD COST BY WET LIME-GYPSUM PROCESS IN JAPAN (1975 $)
(7 years depreciation, 7,000 hours full load operation per year, Oil consumption: 150,000kl/1000MW/year, S: 2.8%, 90% removal. Reheating to 110°C.)

	100MW	500MW
Investment cost ($1,000)	6,600	27,000
Fixed cost ($1,000/year)		
Depreciation	940	3,860
Interest, insurance	470	1,930
Total	1,410	5,790
Running cost ($1,000/year)		
Lime	230	1,140
Oil for reheating ($100/kl)	450	2,230
Power (¢3/kWhr)	400	1,940
Labor	50	50
Maintenance	100	300
Other requirements	20	60
Gypsum	-120	-610
Total	1,130	5,010
Total annual cost ($1,000)	2,540	10,800
Desulfurization cost ($/kl)	16.9	14.4
Desulfurization cost (mil/kWhr)	3.6	3.0

The wet limestone-gypsum process may be more costly in investment, but it is slightly cheaper in FGD annual operating costs than the lime-gypsum process. Indirect lime/limestone processes usually cost 5-20% more than does the lime-gypsum process. Sulfuric acid as a by-product process will cost 20-30% more in either case.

TABLE 19. U. S. A. BATTERY LIMITS CAPITAL INVESTMENT AND ANNUAL COSTS

Power Size: 500MW

Residual Oil (No. 6) = 4.0% Sulfur

Mid 1977 Project Costs

	Total Capital Investment $/KW	Annual Costs Mills/kWh (No Credits)
1. Limestone/Sludge (CaO, $CaCO_3$)	100.02	4.78
2. Lime/Sludge ($Ca(OH)_2$)	94.84	5.00
3. Magox-Sulfur * (MgO)	105.87	5.22
4. Catalyst Oxidation Acid	138.70	4.36
5. Sodium/Sulfur * (Na_2SO_3, $NaOH$, Na_2CO_3)	124.29	6.03
6. Double Alkali/Sludge (Na_2SO_3 + $CaCO_3$ or $Ca(OH)_2$ $(NH_4)_2SO_4$ + $CaCO_3$ $Al_2(SO_4)_3$ + $CaCO_3$)	118.94	5.93
7. Ammonia/Sulfur *	114.52	4.67

* Elemental Sulfur is By-product

A preliminary economic assessment is included in Table 19. It compares the investment and operating costs of commercial FGD facilities with other FGD processes.

SECTION 7

CONCLUSIONS

FGD

Based upon the review of the present Japanese FGD status for residual oil-fired electric utility boilers, several economically feasible approaches and environmentally acceptable FGD processes have demonstrated the effective and efficient process control of sulfur dioxide emissions. However, this is not the case for sulfate particulates or other toxic elements and their compounds both organic and inorganic in the particle size range below 3 micrometers. There are many nitrogen oxide scrubbers that are still in the pilot plant and demonstration stages of development in Japan. It will be two or three years before the final environmental assessment of commercially applicable operations will be completed.

The FGD processes have sulfur dioxide removal efficiencies of 90-98%, overall particulate removal efficiencies of 40 to 80% and the nitrogen oxides removal efficiencies of 50 to 90%.

The flexibility in the design of many FGD processes has broad ranges of capacities to accommodate 200ppm to 50,000ppm SO_2 inlet concentrations to the scrubber without affecting the 90% SO_2 removal efficiency level. Therefore, it is readily apparent that the present U.S.A. Federal NSPS requiring only 75-80% SO_2 removal efficiency may become a more restrictive standard because of current FGD process capability of removing 90 to 98% SO_2.

The overall average particulate removal efficiencies of 85% fail to show the 58% fractional efficiency for fine particulates below the 1 micron level. In other words, the FGD processes fail to remove 42% of a hazardous human health effect of respiratory damage from submicron trace metals and toxic substances.

The nitrogen oxide removal efficiency and FGD process flexibility data will not be available until later next year.

The U.S.A. NSPS standard for particulate control limit of no more than 0.06 grains per dry standard cubic foot of utility boiler exhaust gas when burning liquid fuels can be more restrictive because the current FGD process can remove particulates as low as 0.04 grains per cubic foot of exhaust gas.

Particulate emissions resulting from the combustion of fuel oil are dominated by sub-micron particles which contain most of the mass of many elements. This means that the residence time of these particles in the atmosphere will be much longer than for an equivalent mass of particles emitted by other fossil fueled power plants which typically emit substantially larger particles.

To determine the impact of oil combustion on atmospheric trace-element levels, an accurate analyses of fuel oils will be required. The variation in fuel oil composition will be defined by analysing a wide range of samples. Although most oil-fired power plants have little in the way of pollution control devices, it would be useful to study their effect on the composition.

HDS

Our study has shown HDS to be a commercially-proven, reliable and flexible method of producing a low sulfur fuel oil from reduced crude. Environmentally potential pollutants such as nickel, vanadium, and sulfur are removed from the fuel and converted into saleable by-products. As an example, approximately 230 tons of molten sulfur are produced in desulfurizing a 3.9% sulfur (by weight) Kuwait reduced feed to a 0.8% sulfur product. Eighty to ninety percent of the approximately 65 by wt. ppm metals is retained on the reactor catalyst for possible ultimate reclamation.

The HDS units in Japan have been designed and operated to meet the National and local prefecture air, water and noise emission standards. Emphasis in Japan has been on sulfur oxides (SO_x), oxides of nitrogen (NO_x), particulates and, on a local basis, ammonia (NH_3), hydrogen sulfide (H_2S), carbon monoxide (CO), and nickel and vanadium compounds. Effluent standards for water exist for chemical oxygen demand (COD), suspended solids (SS), oil, pH, phenol, cyanide (CN) and chromium (Cr). Local plant boundary noise standards, usually a maximum of 60dB, exist in many prefectures.

Emission data obtained in Japan was generally limited to SO_2, H_2S, NO_x and NH_3 concentrations in the gaseous streams and H_2S, NH_3, COD and pH in the liquid streams. Information on the feed and products, such as API gravity, pour point and nitrogen and sulfur concentrations, was obtained. The composition of potentially hazardous compounds in the reduced crude will be used in an engineering analysis to determine the possible environmental impact. Since most of the units in Japan are processing Arabian light, the first analysis will be made on this feed. If, upon completion of analysis, sampling is necessary, a Level I program will be designed and executed while the selected units are processing light Arabian reduced crude. This will allow for a comparison of the calculated versus observed data. A residfining unit is ready to operate in this country at Exxon in Baytown, Texas. Information obtained from the unit will be reported as data becomes available.

POX

With over 100 commercial units now in operation, the residual fuel oil gasification process is established as a unit acceptable for the production of low, medium, and high Btu gas at elevated pressures. Alternately, the CO and H_2 can be used for the production of chemicals and petrochemicals by adding additional equipment.

When charging a residual fuel oil priced at $10/bbl and containing 3.5% sulfur, the process can produce an environmentally acceptable gas of 125 Btu/SCF at elevated pressure for approximately $3/MM Btu. Although this price is high for the U.S. at the present time, it should become more economical in the future. The product cost is very sensitive to feed cost, and the price of the gas could be reduced by charging heavier, lower-priced feeds.

GLOSSARY

amine regenerator: A unit used to remove impurities, in the form of H_2S, from the recycle amine stream.

chemically active fluidized bed: A fluidized limestone bed which produces a clean gaseous fuel from heavy high sulfur feedstocks.

Claus unit: A unit which produces sulfur from a mixture of H_2S and SO_2.

crude oil desalting: A process for washing inorganic salts from crude oil and separating the resulting salt water.

economiser exchanger: A heat exchanger in which low temperature heat is recovered.

effluent gas: A gas leaving any vessel or process.

effluent streams: The total material leaving any vessel or process.

flash vessel: A vessel used to separate liquid and gaseous portions of a feed stream by reduction of pressure.

flue gas desulfurization: A process in which sulfur-containing pollutants are removed from a flue gas stream by contact with absorbent liquids.

fractionation: The separation of a mixture into components by partial vaporization and subsequent condensation.

friable slag: Slag that does not cling to other materials but can be readily removed.

hydrodesulfurization: The elimination of sulfur from residual fuel oil by the reaction of sulfur with hydrogen.

IFP: A unit which removes H_2S from the gas leaving a Claus unit. Inter Francis Petrole = French Petroleum Institute.

partial oxidation: Partial combustion of a solid, liquid, or gas. The products of partial oxidation can be oxidized further to complete the combustion.

particulate: Any solid matter, as opposed to a liquid, which is dispersed in a gas.

quench gas: A gas used to control (decrease) the temperature of segments of a reactor.

residfining unit: A hydrodesulfurization unit licensed by Exxon.

residual fuel oil: Thick viscous liquid remaining after separation of light fractions of crude oil.

residual oil gasification: A process in which liquid residual oil is charged and a gas produced.

SCOT unit: A unit which removes residual H_2S from the gas leaving a Claus unit.

Selexol unit: A unit which selectively absorbs H_2S without absorbing appreciable CO_2.

slurry separation: Separation of a suspended solid from a liquid.

"sour" fuel gas: A gas containing hydrogen sulfide (H_2S) which is capable of producing energy when consumed.

tail-gas treater: Control equipment which is added to the end of a process to reduce emissions to acceptable levels.

variably feedstocks: More than one kind of feed to a unit or, alternately, different qualities of the same feed.

waste heat exchanger: Recovery of heat that is normally lost by exchanging it with another stream of lower temperature.